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HIGH-TEMPERATURE STRUCTURAL RESINS

FINAL REPORT

June 1968

8 June 1967 to 8 May 1968

by

Paul M. Hergenrother
Harold M. Levine

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FOREWORD

This report was prepared by Whittaker Corporation, Narmco Research & Development Division, under US Naval Ordnance Contract N60921-67-C-0221. Administration of the contract was under the direction of Mr. Marlin Kinna, with Dr. P. W. Erickson of the US Naval Ordnance Laboratory, Silver Springs, Maryland acting as technical monitor.

The research described in this report was conducted from 8 June 1967 to 8 May 1968. Mr. Paul M. Hergenrother was the principal investigator, with technical supervision being provided by Mr. Harold H. Levine. Those assisting were Mr. Richard T. Rafter, Research Chemist, Mrs. Mary A. Peitz, Senior Research Technician, and Mr. Denver E. Dayton, Senior Research Technician.

ABSTRACT

The work described in this report covers the period from 8 June 1967 to 8 May 1968.

Polyquinoxalines were shown to have outstanding processability which enabled fabrication of laminates having resin matrices with reduced porosity. Excellent laminate and adhesive data were obtained after 200 hours at 600°F or 50 hours at 700°F, both in air and tested at temperature. Initial efforts provided encouraging results on unidirectional composites, using high modulus fibers. Some polymer modification is necessary to remove slight thermoplasticity.

Polyphenylquinoxalines are definitely more stable than polyquinoxalines, when tested under isothermal conditions and demonstrate excellent processability. A sharp increase in glass transition temperature is necessary to exploit this improved stability.

Two polyquinoxalines were tested for compatibility with ONT and HNS II heat resistant explosives at 260°C. Both samples were found to be very compatible.

Samples of both polyquinoxalines were submitted for tests as a potential fiber. Both could be formed into fibers having interesting high-temperature properties; the half ether has somewhat better.

Polybenzothiazoles continued to provide problems in monomer purity.

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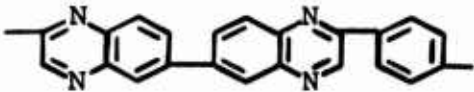
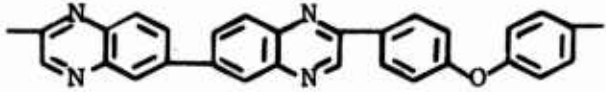
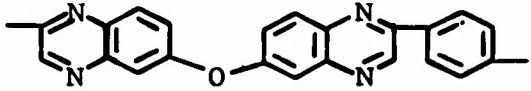
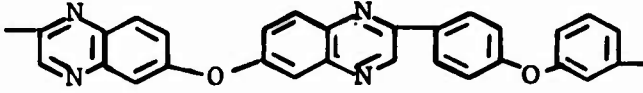
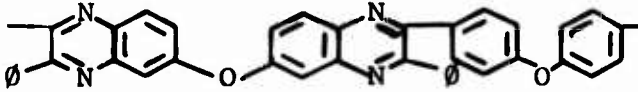
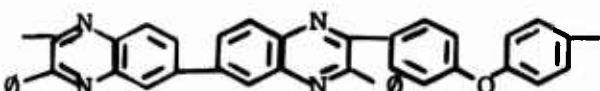
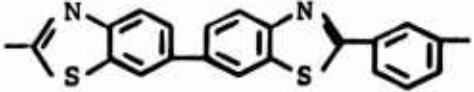
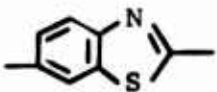
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INTRODUCTION

This report summarizes an investigation directed toward the synthesis and evaluation of thermally stable polymers for potential use in fabricating various end items and devices requiring deep submergence for long time periods. The primary objective of this program was to demonstrate the potential of the polymers as structural materials without embarking on an extensive processing and testing study.

Emphasis was placed on the polyquinoxalines because of their ready processability. The remainder of the effort involved the polybenzothiazoles and initial development of phenyl substituted polyquinoxalines.

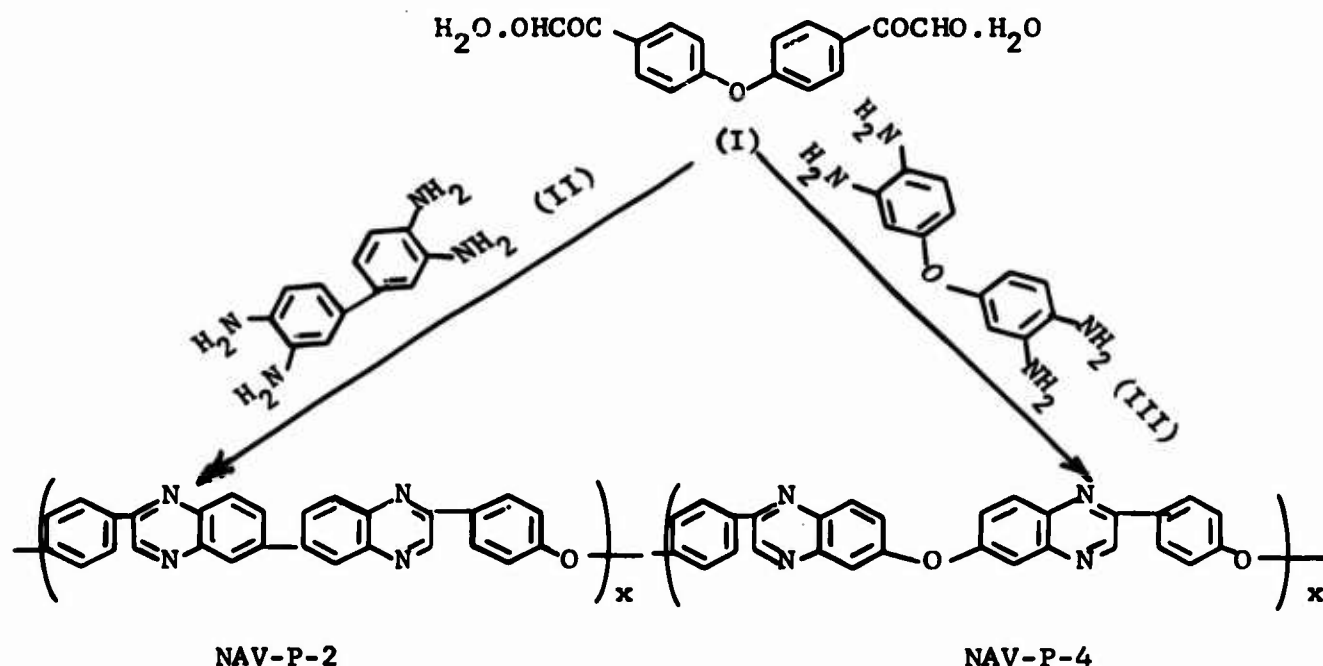
Rather than refer to cumbersome chemical names, abbreviations, or trivial nomenclature, it was decided to apply an arbitrary numbering system for polymers synthesized on this program. Thus, all polymers will be prefixed by NAV-P-___, indicating a polymer prepared with Navy sponsorship.

<u>Polymer Type</u>	<u>Structures</u>	<u>Reactants</u>	<u>Code</u>
Polyquinoxaline		p-PBG & DAB	NAV-P-1
"		4,4'-OBG & DAB	NAV-P-2
"		p-PBG, TADPE	NAV-P-3
"		4,4'-OBG & TADPE	NAV-P-4
"	Copolymer	3:1 4,4'-OBG: p-PBG & DAB	NAV-P-5
Polyphenylquinoxaline		4,4'-OBB + TADPE	NAV-P-10
"		4,4'-OBB + DAB	NAV-P-11
Polybenzothiazole		DPIP & DMB	NAV-P-20
"		AMB	NAV-P-21

DISCUSSION

POLYQUINOXALINES

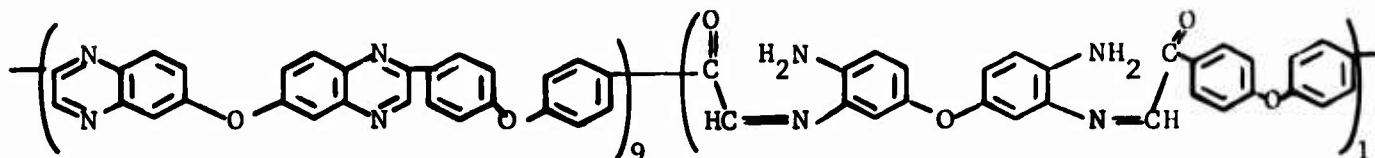
Work with this polymer family constituted the bulk of the past year's program. Almost the entire polyquinoxaline effort was directed toward two structures, NAV-P-4 (diether) and NAV-P-2 (monoether). These polymers were synthesized as follows:



For details on previous efforts, the reader is referred to the previous final report.⁽¹⁾

Perhaps the most significant factor contributing to polymer performance and outstanding processability is the ability to synthesize a high molecular weight resin which still retains solubility and fusibility. Polybenzimidazoles must be processed with prepolymer having a D.P. averaging between 2-3; consequently, there is a high weight percent loss of condensation volatiles, which leads to a host of evils. Polyimides are processed as high molecular weight polyamic acids and must lose 2 moles of water per mer unit in order to achieve its final, ring-closed, stable imide structure. However, since polyquinoxalines were still processable despite an inherent viscosity greater than 1.0, with a condensation volatiles evolution as low as 0.5%, it is reasonable to assume that the polymer has very few end groups and unclosed rings. Thus, the following structure will form the final polyquinoxaline with only an 0.8% loss of condensation volatiles as water; indicating that about 90% of theoretical ring closure has occurred.

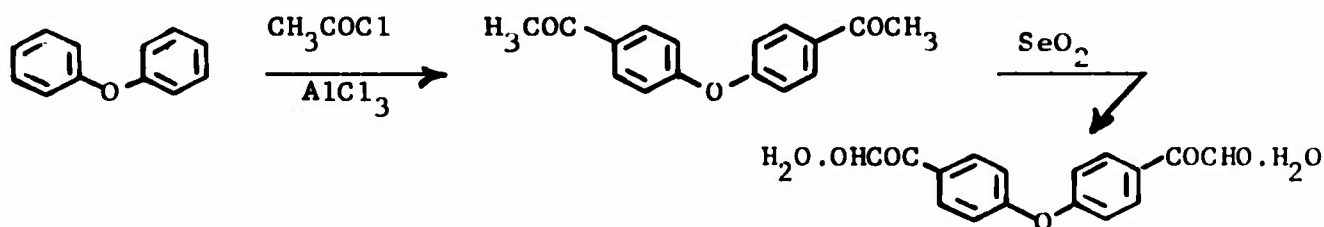
(1) P. M. Hergenrother and H. H. Levine, High Temperature Structural Resins, Final Report Contract NOW 66-0144-c, Narmco Research & Development Division, San Diego, California, July 1966, 36 pp.



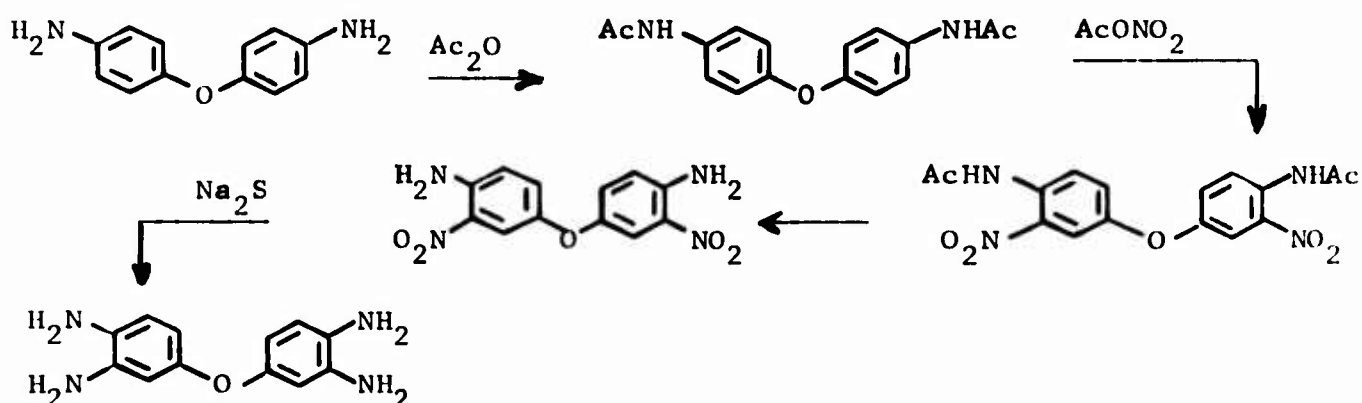
Another factor contributing to the eminent processability may also be the plasticizing effect of m-cresol. Once wetting has been achieved during prepreg preparation, it is now possible to remove virtually all of the m-cresol because heat can be used without further advancement of the already high molecular weight resin.

Monomer Synthesis

The necessary monomers, I and III, had to be synthesized, while II was purified from the commercially available compound. Synthesis of I was successfully scaled-up to provide about 3.5 lb of polymer grade reactant. This procedure, shown below, has demonstrated its reliability from batch to batch.



The synthesis of III was also improved and scaled-up to provide about 1.5 lb of pure tetraamine, also in reproducible fashion.



In actual practice, the above reaction sequence is only a two-step process, since only the final product and the nitrated acylamine are isolated.

Polymerization Reactions

A brief study was undertaken on the synthesis of NAV-P-4 because of variations in polymer processability and reproducibility.

When a m-cresol solution of I was used in polymer synthesis under the indicated reaction conditions, poor polymer was obtained. However, when I was used as a m-cresol slurry, good polymer was formed as indicated by its inherent viscosity, isothermal weight loss, and film forming ability. The difference was apparently due to a concentration factor; too much I in solution reacts rapidly with the III to yield a branched or crosslinked polymer, as indicated by insolubility, isothermal weight loss, and film of the final polymers. Perhaps the slow addition of the I solution would provide a more orderly and controlled reaction to yield good polymer. Regardless, this study has provided a method for obtaining reproducible processable polymer, and a basic synthesis study at this time would fail to contribute significantly to the overall objective of the program.

Relatively large quantities (1100 g) of polymer for application work were conveniently prepared in m-cresol at 20% solids concentration using the general procedure for experiment No. PH-6-57-A in Table I. The m-cresol solution was directly used in application work for prepreg or tape preparation.

The prepolymer isolated by quenching a portion of the m-cresol solution with methanol followed by drying the isolated fibrous prepolymer at $170^{\circ}\pm 10^{\circ}\text{C}$ under pump vacuum for 1 hour generally exhibited an inherent viscosity (η_{inh} , 0.5% H_2SO_4 solution at 25°C) of 0.5 to 1.0 with a polymer melt temperature (PMT) of 260°C to 320°C . Advancement of the prepolymer by heating for 1 hour at 400°C in nitrogen provided final polymer which generally exhibited an inherent viscosity of >1.5 . The final polymer is somewhat thermoplastic as evidenced by placing a powdered sample of the polymer on preheated press platens at 800°F (427°C) and applying 2000 psi to form a clear extremely tough polymer disk. The results of this study are shown in Table I. It is obvious that the mode of reaction causes large differences in polymer and prepolymer behavior. Noteworthy are the high prepolymer inherent viscosities associated with PMT values of 265°C , which result in excellent processability.

Laminate Studies

NAV-P-4 (Diether)

Since prior work⁽¹⁾ under Navy sponsorship demonstrated the potential of polyquinoxalines as a useful high-temperature resin, work was directed toward the fabrication of glass reinforced laminates utilizing the technology acquired during the previous contract year.

Several diether, 7-ply laminates and one 14-ply laminate were fabricated from solution-coated prepreg. As shown in Table II, the prepreg was

TABLE I
PREPARATION OF NAV-P-4

Experiment No.	Addition ¹	Prepolymer ²			Final Polymer ⁶			Film ⁸
		η_{inh} , dl/g ³	PMT, °C ⁴	Volatile Content, % ⁵	η_{inh} , dl/g	Isothermal Wt Loss (%) ⁷		
						@ 600°F in air after 100 hr	200 hr	
PH-6-56-A	III slurry to I solution	0.50	~270	5.3	Insol.	4.5	14	Fails fingernail crease
PH-6-56-B	I solution to III slurry	0.51	~260	3.8	Insol.	23	44	Fails fingernail crease
PH-6-57-A	I slurry to III slurry	0.73	~265	1.9	1.68	0.5	2.0	Tough & flexible
PH-6-57-B	III slurry to I slurry	0.68	~265	1.7	1.59	1.0	2.0	Tough & flexible

¹ Addition time ~3 minutes @ 55°C±3°C, followed by stirring to 75°±3°C during 4 hr; reaction scale 0.10 mole and concentration of 20% solids in m-cresol.

² Isolated by dilution with methanol and drying 1 hr @ 170°C under pump vacuum.

³ Inherent viscosity (0.5% H₂SO₄ @ 25°C).

⁴ Polymer melt temperature.

⁵ Determined by heating for 1 hr @ 400°C under nitrogen.

⁶ 1 hr @ 400°C under nitrogen.

⁷ Particle size < 30 mesh.

⁸ Prepared by doctoring m-cresol solution onto glass plate and drying to 200°C during 8 hours.

dried to three different volatile content levels to study the effect of this variation on processing characteristics of the prepreg and also on the final properties of the resulting composites. The effect of volatile content was expected to be most pronounced in the aging performance of the laminates, since more volatiles generally means higher porosity in the resin matrix which would be more prone to oxidative degradation. However, although initial test data for short-time aging are highly encouraging, the test specimens failed to withstand aging at 600°F for 200 hours in air and at 700°F for 50 hours in air. This was surprising, since laminates fabricated during the previous contract year gave average average flexural strength and modulus values of 32,330 psi and 2.36 psi x 10⁶, respectively, at 700°F after 50 hours at 700°F in air. The poor aging performance of the laminates was tentatively attributed to the porosity of the resin matrix, resulting from limited flow during laminate fabrication. The laminates fabricated from prepreg having a volatile content of 1.43% exhibited essentially no flow during processing, whereas those fabricated from prepreg having a higher volatile content (9.85% and 5.07%) exhibited only minimum flow. This is further emphasized in the calculated void contents of 8.3% and 4.1% for laminates fabricated from prepreg containing 1.43% and 9.85% volatiles, respectively. The prepreg with the higher volatile content exhibited somewhat better flow during processing which permitted the volatiles to escape more readily resulting in a higher density laminate. However, the porosity of the laminate was still apparently too high to permit good aging capability.

The limited flow of the resin was further verified by examining a sample of the polymer isolated by quenching a portion of the m-cresol solution with methanol and drying the isolated polymer for 3 hours at 170°±10°C under pump vacuum. The high drying temperature was required to remove the tenaciously held m-cresol, even though partial advancement of the polymer occurred. The isolated polymer exhibited an inherent viscosity of 1.60 and a polymer melt temperature of 330°C, although no flow was observed. The polymer in the m-cresol solution had an inherent viscosity of less than 1.60, but this was still too high a molecular weight to permit good flow of the resin on the prepreg. During the preparation of the polymer solution, the viscosity increased faster than anticipated when highly pure starting material was used. This required the transfer of the reaction mixture of a large Waring blender to achieve adequate mixing. The stirring action of the blender caused the temperature of the m-cresol solution to reach 85°C, which resulted in substantial advancement of the polymer. Another batch of diether polyquinoxaline will be prepared under milder conditions.

The effect of postcuring laminates fabricated under essentially identical conditions as whole laminates and as specimens was studied. The test results for the two different postcure methods were relatively comparable under all test conditions except at 1000°F after 10 minutes at 1000°F. The flexural strength of the laminates postcured as specimens (Nos. 44 and 45) were higher than those postcured as whole laminates (Nos. 42 and 43). For example, Laminate 45 gave flexural strength of 32,800 psi at 1000°F after 10 minutes at 1000°F, while Laminate 43, fabricated under essentially identical conditions, gave a value of only 10,200 psi under the same test

TABLE II
NAV-P-4 LAMINATE DATA
Preliminary Processing Study

Laminate Fabrication

Resin: Batch PH-6-39

Prepreg: Solution coated using m-cresol solution containing ~ 16.4% solids dried to the indicated volatile content

Carrier: 1581 HTS-994

Cure Cycle: 1 hr @ 750°F under indicated pressure in air, cooled under pressure

Postcure: 4 hr each @ 400°F & 450°F, 11 hr @ 500°F, 4 hr each @ 600°F, 700°F, & 750°F in nitrogen except Laminate No. 40, postcured 30 hr @ 600°F in air

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Pressure, psi	Postcured as	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
39	4.8 x 6 x 7 ply	1.43	1000	Specimen	29.4	1.79	8.3
40	↓	↓	↓	↓	27.2	1.84	--
41	↓	↓	500	↓	31.0	1.80	--
42	4.5 x 6 x 7 ply	9.85	200	Laminate	26.6	1.85	--
43	↓	5.07	↓	↓	30.5	1.78	--
44	↓	9.85	↓	Specimen	27.0	1.88	4.1
45	↓	5.07	↓	↓	28.4	1.85	--
46	4.5 x 6 x 14 ply	9.6	↓	Laminate	27.6	--	--

* Determined by burnout.

TABLE II (Continued)

Test Information

Laminate No.	Flexure					Strength, psi and Modulus, psi x 10 ⁶				
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F	600°F after 400 hr @ 600°F			
39	72,700 3.03	36,600 2.76	Burned out	12,100 1.77	44,300 2.95	Burned out	--			
Avg	<u>76,200</u> 3.25	<u>41,200</u> 2.92		<u>14,900</u> 2.07	<u>51,900</u> 3.24					
Wt. Loss	74,500 3.14	38,400 2.83		18,500 2.10	47,300 2.94					
		0.405%			0.059%					
40	87,100 3.74	10 min @ 700°F	--	--	--	--	--			
Avg	<u>87,100</u> 3.74	<u>16,500</u> 1.23								
		<u>14,500</u> 1.07								
		<u>15,500</u> 1.15								
41	56,600 3.12	44,000 3.39	Burned out	32,800 2.96	44,600 3.14	Burned out	--			
Avg	<u>81,700</u> 3.35	<u>38,000</u> 2.81		<u>17,100</u> 2.17	<u>50,300</u> 3.27					
	<u>80,000</u> 3.45	<u>41,500</u> 3.11		<u>15,500</u> 2.68	<u>51,000</u> 3.12					
Wt. Loss	72,800 3.31	41,200 3.10		21,800 2.60	48,600 3.18					
		0.425%			0.104%					
42	82,600 3.66	41,600 3.14	Burned out	17,800 2.48	59,600 3.39	105 hr @ 600°F	--			
Avg	<u>87,000</u> 3.49	<u>44,500</u> 3.50		<u>15,600</u> 3.02	<u>40,500</u> 2.78	<u>4,610</u> 1.12				
Wt. Loss	84,800 3.59	44,800 3.45		15,000 2.63	50,100 3.09	<u>6,140</u> 1.90				
		0.82%			0.62%	<u>3,920</u> 1.20				
						<u>4,890</u> 1.41				
43	68,500 3.10	37,200 2.70	Burned out	12,100 1.77	54,900 3.33	105 hr @ 600°F	--			
Avg	<u>77,600</u> 3.27	<u>38,500</u> 2.92		<u>11,000</u> 2.20	<u>48,500</u> 3.17	<u>4,060</u> 1.02				
Wt. Loss	73,100 3.19	37,400 2.85		10,200 1.74	51,700 3.25	<u>4,090</u> 1.03				
		0.96%			0.69%	<u>4,280</u> 0.82				
						<u>4,140</u> 0.96				
						16.3%				

TABLE II (Continued)

Laminate No.	Flexural Strength, psi and Modulus, psi x 10 ⁶						
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F	600°F after 400 hr @ 600°F
44 Avg Wt. Loss	84,600	3.30	Burned out	37,200	2.69	* Poor - no tests	--
	106,000	4.24		30,200	2.78		
	95,300	3.77		24,800	2.78		
				30,700	2.75		
						0.050%	16.3%
45 Avg Wt. Loss	81,900	3.66	Burned out	37,600	2.69	Poor - no tests	--
	99,400	4.31		35,500	2.82		
	90,700	3.99		25,400	2.79		
				32,800	2.77		
						0.011%	16.1%
46 Avg Wt. Loss	89,400	4.14	Burned out	--	--	--	--
	97,800	4.37					
	80,200	3.60					
	89,100	4.04					

* Burned out after 105 hr @ 600°F.

conditions. It is anticipated that postcuring whole laminates will require greater care and longer schedules.

Several laminates as large as 9 in. x 12 in. x 14 plies were fabricated from solution-coated prepreg. Cure and postcure conditions were varied in an attempt to obtain near-optimum process conditions. Laminates fabricated under identical conditions from prepreg that was dried under essentially the same drying cycle exhibited different behavior during postcure. For example, as shown in Table III, Laminates 57, 58, and 60 were cured under essentially identical conditions, except Laminate 60 was cured in a nitrogen atmosphere. The postcure schedule was essentially the same as the lower temperatures and differed only in atmosphere. Laminate 57 was successfully postcured, whereas Laminates 58 and 60 exhibited pronounced blowing during the postcure. As previously mentioned for the half ether system, blowing was initially observed about 450°F. Blowing during postcure with the diether system was less drastic than that observed for the half ether PQ. This was apparently due to better flow characteristics of the diether PQ allowing more volatiles to escape as suggested by the pressure employed in laminate fabrication. Resin flow is influenced by small but important variations in prepreg volatile content which accordingly indicate the degree of advancement of the resin. Apparently adequate resin flow and/or a greater porosity in the resin matrix resulting from higher prepreg volatiles permitted the volatiles to escape during the fabrication and/or postcure of Laminate 57 but failed to operate properly when Laminates 58 and 60 were fabricated from prepreg containing less volatiles than Laminate 57 prepreg.

Utilizing the information gained from work with NAV-P-2 (described later), a longer cure time at 750°F was employed to fabricate laminates (Nos. 59, 61, 62, and 63) which were successfully postcured. Average flexural strengths (and moduli) are shown in Table III. The air postcure through 200 hours at 600°F failed to overcome the thermoplasticity of the resin, as indicated by the thermoplastic failure of specimens tested at 700°F after 1 hour at 700°F following a postcure in air for 200 hours at 600°F.

Laminates 70, 71, and 72 were fabricated under mild conditions (450°F to 700°F under 50 psi pressure) from solution-coated prepreg containing 13.9% volatiles. Although the laminates exhibited relatively poor performance at elevated temperatures, it was highly encouraging to have fabricated laminates under such mild conditions. The poor quality of the laminates is indicated by the low density and high void content.

Laminates 74, 75, and 76 were given the same mild cure, but 200 psi was used in place of 50 psi pressure, because it was anticipated that higher pressure would yield composites with higher density and lower void content. While these last three laminates (Nos. 70, 71, and 72) were given a maximum postcure temperature of 750°F, the schedule was somewhat different. The test data indicated that void content and bulk density were definitely improved by the increased processing pressure (200 psi). The 800°F postcure improved the 1 hour at 700°F data but was destructive on 50 hours at 700°F aging (see Table IV).

TABLE III

NAV-P-4 LAMINATE DATA
PRELIMINARY PROCESSING STUDY

Laminate Fabrication

Resin: Batch PH-6-59-S

Prepreg: Solution coated using m-cresol solution containing 20% solids, 3 dip coats,
first two coats forced air dried 10-15 min @250°F, final coat forced air dried
1 hr @ 250°F followed by vacuum dry 2 hr @ 330°C-385°C to indicated volatile content.

Carrier: 1581 HTS (994)

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin** Content, %	Bulk Density, g/cc	Calculated Void Content, %
57	4.5 x 6 x 7 ply	2.50	1 hr @ 750°F, 200 psi	A	--	34.4	1.69	8.7
58	↓	1.92	↓	↓	Blowing	--	--	--
59	9 x 12 x 14 ply	1.83	4 hr @ 750°F, 200 psi (N ₂)	B	--	36.3	1.75	4.4
60	4.5 x 6 x 7 ply	1.83	1 hr @ 750°F, 200 psi (N ₂)	C	Blowing	--	--	--
61	↓	1.77	4 hr @ 750°F, 200 psi (N ₂)	D	--	37.3	1.74	4.4
62	4.5 x 6 x 14 ply	1.77	4 hr @ 750°F, 200 psi	D	--	38.6	1.72	4.4
63	4.5 x 6 x 7 ply	3.16	↓	E	--	39.4	1.68	6.2

* A 4 hr each @ 400° & 450°F, 10 hr @ 500°F, 8 hr @ 600°F, 4 hr each @ 700°F & 750°F in nitrogen.

B 20 hr each @ 400°F, 450°F, 500°F, 550°F, 6 hr @ 600°F, 14 hr @ 650°F, 4 hr each @ 700°F & 750°F in nitrogen.

C 4 hr each @ 400°F & 450°F, 15 hr @ 500°F and various times @ 600°F in air.

D 4 hr each @ 400°F & 450°F, 12 hr @ 500°F, 8 hr @ 550°F, 4 hr each @ 600°F, 700°F & 750°F in nitrogen.

E 22 hr each @ 400°F, 450°F, 500°F, 550°F then various times @ 600°F in air.

** Determined by burnout.

TABLE III (Continued)

Test Information

Laminate No.	Flexural Strength, psi and Modulus, psi x 10 ⁶							
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	700°F after 100 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F	
57	101,800 3.64	43,800 2.48	14,400 1.03	--	13,600 2.54	64,500 2.94	30,100 2.13	
	110,100 3.66	36,500 2.30	15,600 1.10		14,300 2.50	49,300 2.39	16,900 1.70	
	106,500 3.43	32,700 1.86	5,900 0.80		17,600 2.62	64,300 2.82	22,400 1.99	
Avg	106,100 3.58	37,700 2.21	12,000 0.98		15,200 2.55	59,400 2.72	23,100 1.94	
Wt. Loss		0.08%	19.4% *			0.08%	11.5%	
58		Blown during postcure						
59	105,400 3.83	8,400 0.96	15,300 1.73	1,760 0.48	18,100 2.39	Burned out**	34,100 2.39	
	100,900 3.76	15,400 1.47	24,100 1.97	7,440 1.22	20,200 2.80		43,000 2.76	
	104,600 3.90	8,660 0.89	23,300 1.95	6,940 1.21	19,100 2.60		41,500 2.61	
Avg	103,600 3.83	10,800 1.10*	20,900 1.88	5,380 0.96			39,500 2.59	
Wt. Loss		0.41%	7.14%	20.6%			5.74%	
60		Blown during postcure						
61	83,800 3.04	40,700 2.64	30,200 2.30	--	20,900 2.46	51,300 2.84	30,400 2.43	
	96,500 3.81	33,800 2.24	23,400 1.28		17,100 1.96	52,300 2.20	30,600 2.73	
	92,800 3.48	36,900 2.02	22,700 1.71		17,600 2.15	54,400 2.16	30,800 2.29	
Avg	91,000 3.44	37,100 2.30	25,400 1.76		18,500 2.28	52,700 2.40	30,600 2.48	
Wt. Loss		0.24%	14.3%			0.21%	9.3%	
62	80,800 3.45	13,200 1.34	26,700 2.38	--	12,900 2.47	--	--	
	93,800 3.92	24,000 2.19***	27,200 2.27		7,420 2.02			
Avg	87,300 3.68	19,600 1.82	27,300 2.29		10,200 2.24			
Wt. Loss		18,900 1.78	27,100 2.31					
		0.17%	8.4%					

* Thermoplastic failure.

** Burned out after 1 hr @ 1000°F.

*** Porous.

TABLE III (Continued)

Laminate No.	Final Postcure (in Air)	Flexural Strength, psi and Modulus, psi x 10 ⁶	
		RT	700°F after 1 hr @ 700°F
63 Avg. Wt. Loss	8 hr @ 600°F	73,500 2.60	11,700 0.96
		101,200 3.45	18,000 1.14
		87,400 3.02	15,000 1.05* 0.08%
Avg. Wt. Loss	50 hr @ 600°F	78,900 3.22	12,000 1.31
		89,900 3.15	19,200 2.24
		84,400 3.18	15,600 1.68* 0.08%
Avg. Wt. Loss	100 hr @ 600°F	71,900 3.13	16,500 1.28
		82,800 3.33	20,100 1.89
		77,350 3.23	18,300 1.59* -0-
Avg. Wt. Loss	150 hr @ 600°F	57,800 2.44	16,800 1.28
		65,000 2.74	18,000 1.72
		61,400 2.59	17,400 1.50* 0.79%
Avg. Wt. Loss	200 hr @ 600°F	44,500 1.45	13,400 0.94
		43,600 1.73	19,800 1.34
		44,100 1.59	16,600 1.14* 1.31%

* Thermoplastic failure.

TABLE IV

NAV-P-4 LAMINATE DATA
MILD CURE STUDY

Laminate Fabrication

Resin: Batch PH-6-59-S

Prepreg: Solution coated using m-cresol solution containing 20% solids, 3 dip coats, first two coats dried 10-15 minutes and final forced air dried 1 hr @ 250°F for all laminates.

Carrier: 1581 HTS-994

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
70	4.5 x 6 x 7 ply	13.9	10 min @ 450°F, 50 psi, 1 hr @ 700°F, 50 psi	F	4 of 16 specimens blown	38.3	1.51	16.1
71			10 min @ 450°F, 50 psi, 4 hr @ 700°F, 50 psi	F	No blowing	39.0	1.59	11.2
72	4.5 x 6 x 14 ply		↓	F	No blowing	37.4	1.64	9.4
74	4.5 x 6 x 7 ply		10 min @ 450°F, 200 psi, 4 hr @ 700°F, 200 psi	A & C	--	29.1	1.76	8.8
75			10 min @ 500°F, 200 psi, 4 hr @ 700°F, 200 psi	A & C	--	28.2	1.73	9.8
76	4.5 x 6 x 14 ply		↓	C	--	23.0	1.86	7.9

* By burnout.

A 4 hr each @ 400°F & 450°F, 10 hr @ 500°F, 8 hr @ 550°F, 4 hr each @ 600°F, 650°F, 700°F, & 750°F in nitrogen.
C A + 2 hr @ 800°F in nitrogen.
F 20 hr @ 400°F, 20 hr @ 440°F, 20 hr @ 500°F, 20 hr @ 600°F, 1.5 hr @ 650°F, 1.5 hr @ 700°F, 4 hr @ 750°F in nitrogen.

TABLE IV (Continued)

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶						
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F	1000°F after 1000 hr @ 1000°F
70 (F)	80,900 2.86 93,000 2.82 87,000 2.84	10,200 0.76 11,100 0.92 10,650 0.84**	15,800 1.30 12,200 1.32 15,000 1.40 14,300 1.34	1,780 0.38 3,980 0.83 2,880 0.61	19,900 0.97 15,300 1.08 17,600 1.02	13,500 1.39 16,800 1.33 20,700 1.63 17,000 1.45	Burned out
Wt. Loss	--	--	--	--	--	--	--
71 (F)	82,700 2.75 98,000 3.17 90,400 2.96	13,200 0.98 16,800 1.20 16,100 1.21 15,400 1.13**	15,100 1.45 18,500 1.49 15,600 1.34 16,400 1.43	4,410 0.83 4,190 0.58 4,180 0.70 4,260 0.70	18,800 1.45 19,600 1.45 16,400 1.25 18,300 1.38	20,500 1.79 14,800 1.42+ 20,000 1.76 18,400 1.66	Burned out
Wt. Loss	--	--	--	--	--	--	--
72 (F)	90,800 3.21 85,100 2.94 88,000 3.08	12,400 1.16 15,400 1.41 13,700 1.19 13,800 1.25**	15,400 1.64 14,200 1.57 11,400 1.49 13,700 1.57	5,260 0.78 5,030 0.96 5,140 0.87	--	--	--
Wt. Loss	--	--	--	--	--	--	--
74 (A)	81,700 2.92+ 137,100 5.02 114,800 4.26 111,200 4.07	47,700 3.12 29,100 2.24 38,400 2.68	33,000 1.88 31,500 2.15 16,500 1.00 27,000 1.68	14,700 2.25 14,500 2.06 14,600 2.16	--	--	--
Wt. Loss	--	0.04% 11.5%	--	--	--	--	--
74 (C)	94,300 4.06 85,100 3.89+ 91,800 3.64 90,400 3.86	51,500 3.65 49,600 3.01 50,600 3.33 Nil	Burned out 20.0%	17,600 2.41 12,400 1.77+ 15,000 2.09	--	--	--
Wt. Loss	--	--	--	--	--	--	--

TABLE IV (Continued)

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶						
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F	1000°F after 1 hr @ 1000°F
75 (A)	98,800 3.33	35,200 2.70	29,800 1.98	17,600 2.46	--	--	--
	115,000 4.29	37,200 3.01	22,500 1.73+	14,300 2.73			
	112,000 3.96	36,200 2.86	26,600 1.83	16,000 2.60			
Avg	108,600 3.86	0.04%	10.7%	--			
Wt. Loss	--						
75 (C)	92,800 3.52	54,200 3.68	Burned out	11,900 2.06	--	--	--
	75,600 3.58+	52,000 3.71		12,100 1.81			
	98,100 4.50	53,100 3.70		12,000 1.94			
Avg	89,000 3.87	0.01%	17.7%	--			
Wt. Loss	--						
76 (C)	93,200 4.82	46,000 3.92	10,600 1.99	16,700 3.15	--	--	--
	90,000 4.80	52,100 4.02	31,300 2.79	21,400 3.35			
Avg	91,600 4.81	49,000 3.97	21,000 2.39	19,000 3.25			
Wt. Loss	--	Nil	15.4%	--			

+ Edge specimen.

** Thermoplastic failure.

Laminates 80, 81, and 82 were given a mild cure with the temperature extended from 700°F to 750°F (see Table V). This definitely increased performance after 1 hour at 700°F, but aging after 50 hours at 700°F was poorer. Laminates 87, 88, and 89 were made to determine properties when postcured as entire laminate and effect of Kraft paper bleeder. Unfortunately, the data are not comparable to Laminates 80, 81, and 82: where resin contents were equivalent, void contents were greatly different. Note that Laminate 87 which had highest resin content and lowest voids, gave the best all-around data for the three laminates postcured as total laminate and certainly equivalent to postcured flexural specimens given the longer postcures but having higher void contents. Again, these data indicate the need for caution in data interpretation.

NAV-P-2 (Monoether)

It was decided in last year's work⁽¹⁾ that the laminating effort should be concentrated on the NAV-P-4 system because, in addition to stability equivalent to the NAV-P-2 system, it provided better and easier processability. However, some effort was expended on NAV-P-2 development.

The data given in this section definitely indicate that the monoether processability was equal to that of the diether, and that laminate properties appeared to be better. Use of the monoether is advantageous from cost and simplicity since commercially available 3,3'-diaminobenzidine is used in place of 3,3',4,4'-tetraaminodiphenyl ether which must be synthesized.

The preparation of NAV-P-2 was carefully controlled and afforded a relatively low molecular weight polymer in *m*-cresol which permitted prepreg preparation and, subsequently, relatively low pressure (200 psi) for laminate fabrication. This was a definite improvement, since work during the previous contract year required high pressure (>1000 psi) to fabricate laminates. However, blowing in postcure was a major problem encountered with the half-ether PQ laminates during the previous contract year. The laminates were cut into specimens and are being postcured at the writing of this report. Some blowing has been observed at 450°F for the 14-ply specimens.

A sample of NAV-P-2 was isolated and dried, as previously described. The resulting yellow polymer had an inherent viscosity of 0.98.

Several 7-ply and 14-ply laminates were fabricated, as shown in Table VI. A series of laminates (Nos. 47 through 53) was initially fabricated from solution-coated prepreg having different volatile contents. Although blowing during the postcure was observed for all the laminates, only slight blowing was observed for Laminate 53, and the degree of blowing for Laminate 52 was less than that of Laminates 47 through 51. It was surprising to observe more blowing in Laminate 52 than in Laminate 53, since there were less volatiles evolved during the fabrication of the former laminate. The initial indication of blowing was observed at 450°F and increased progressively with the postcure. As determined during

TABLE V

NAV-P-4 LAMINATE DATA
MILD CURE STUDY

Laminate Fabrication

Resin: Batch PH-6-65-S

Prepreg: Solution coated using m-cresol solution containing 20% solids; 3 dip coats forced air dried 10, 15, and 60 minutes @ 250°F respectively.

Carrier: 1581-HTS-994

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
80	4.5 x 6 x 7 ply	8.4	10 min @ 450°F, 200 psi, 4 hr @ 750°F, 200 psi	A & B	--	23.5	1.78	11.9
81			10 min @ 450°F, 200 psi, 4 hr @ 700°F, 200 psi	A & B	--	22.5	1.78	12.3
87			10 min @ 450°F, 200 psi, 4 hr @ 750°F, 200 psi	A As laminate	Laminate very porous	24.8	1.92	4.0
88	4.5 x 6 x 14 ply		+ Kraft paper bleeder		Laminate slightly porous	21.8	1.88	7.8
89					Laminate fairly porous	20.5	1.90	8.2

* By burnout.

A 4 hr each @ 400°F & 450°F, 10 hr @ 500°F, 8 hr @ 550°F, 4 hr each @ 600°F, 650°F, 700°F, & 750°F in nitrogen.

B A + 8 hr @ 750°F in nitrogen.

TABLE V (Continued)

Test Information

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶				
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	
80 (A)	118,400 4.47	55,200 3.55	29,900 1.83	26,100 3.20	
	106,400 3.76	54,000 3.38	38,300 2.41	20,900 2.51	
	117,100 4.49	54,600 3.46	30,300 2.02	23,500 2.86	
Avg	114,000 4.24		33,000 2.09		
Wt. Loss	--	0.04%	9.0%	--	
80 (B)	108,900 4.48	77,600 4.05	24,000 1.39	23,200 2.82+	
	106,200 4.13	71,400 4.15	23,500 1.33	29,100 3.40	
	89,200 3.59+	74,500 4.10	23,500 1.38	26,200 3.11	
Avg	101,400 4.07		23,700 1.37		
Wt. Loss	--	0.06%	11.1%	--	
81 (A)	119,300 4.61	48,200 2.86	38,600 2.59	24,000 3.16	
	121,500 4.25	45,900 2.94	40,000 2.44	22,800 2.78	
	120,400 4.43	47,000 2.90	34,600 2.45	23,400 2.97	
Avg	--	0.04%	8.2%	--	
Wt. Loss	--				
81 (B)	118,800 4.91	68,200 3.96	34,280 1.59	32,300 3.47	
	115,000 4.29	67,700 4.06	32,100 1.56	26,500 3.49	
	116,900 4.60	68,000 4.01	28,500 1.55	29,400 3.48	
Avg	--	0.08%	10.5%	--	
Wt. Loss	--				
87 (A)	106,800 4.56	61,600 3.63	38,800 2.27	33,100 3.11	
	116,200 4.99	54,400 3.30	39,900 3.57	27,600 3.17	
	111,700 5.06	51,700 3.54	28,600 2.04	28,700 3.33	
Avg	111,500 4.87	55,900 3.49	35,750 2.62	29,800 3.20	
Wt. Loss	--	0.21%	10.3%	--	
Postcured as 7 ply lam.					

TABLE V (Continued)

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶			
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F
88 * (A)	83,500	3.45+	5,200	--
	108,900	4.66	1,815	0.88
	102,000	4.70	2,950	0.52
	98,100	4.27	3,320	0.70
	Wt. Loss	--	12.1%	--
89* (A)	65,300	3.26+	56,100	3.94
	91,800	4.42	60,800	4.02
	90,000	4.33	58,400	3.98
	82,400	4.00	0.44%	--
	Wt. Loss	--	Delaminated during heat age	16.1%

+ Edge specimens.

* Postcured as 14 ply laminate.

TABLE VI

NAV-P-2 LAMINATE DATA
PRELIMINARY PROCESSING STUDY

Laminate Fabrication

Resin: Poly-2,2'-(p,p'-oxydiphenylene)-6,6'-biquinoxaline (half ether PQ, PH-6-48-6)

Prepreg: Solution coated using m-cresol solution containing 18% solids; 3 dip coats, first two coats forced air dried 10-15 min @ 250°F, final coat forced air dried 1 hr @ 250°F and the following; for laminates 47 through 51, 1.5 hr @ 290°F±10°F under vacuum; for laminates 52 and 54 through 56, 16 hr @ 392°F±20°F under vacuum, for laminate 53, 6.5 hr @ 392°F±20°F under vacuum.

Carrier: 1581 HTS(994)

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
47	4.8 x 6 x 7 ply	3.96	1 hr @ 750°F 150 psi	A	Blowing	--	--	--
48	↓	↓	1 hr @ 750°F, 200 psi	↓	↓	--	--	--
49	↓	↓	1 hr @ 750°F 500 psi	↓	↓	--	--	--
50	4.8 x 6 x 14 ply	↓	↓	↓	↓	--	--	--
51	↓	↓	↓	↓	↓	--	--	--
52	4.8 x 6 x 7 ply	1.30	↓	↓	↓	--	--	--
53	↓	2.52	↓	↓	↓	--	--	--
					Very slight blowing	37.2	1.49	18.1
54	4.5 x 6 x 7 ply	1.70		B	Blowing	--	--	--

TABLE VI (Continued)

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
55	4.5 x 6 x 7 ply	1.70	4 hr @ 750°F, 500 psi	B	--	36.5	1.66	8.8
56	↓	↓	1 hr @ 800°F, 500 psi	↓	--	36.8	1.73	4.9

A 4 hr each @ 400°F and 450°F, 12 hr @ 500°F, 4 hr each @ 600°F, 700°F, & 750°F in nitrogen.

B 22 hr @ 400°F, 23 hr @ 450°F, 23 hr @ 500°F, 20 hr @ 600°F, 4 hr each @ 700°F & 750°F in nitrogen.

* By burnout.

Test Information

Laminate No.	Flexural Strength, psi and Modulus, psi x 10 ⁶							
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	700°F after 100 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F	
53	67,200 2.26	9,370 0.38	22,200 2.02	Blown 10 mil @ 500°F during postcure	13,100 2.04	24,300 0.66	31,200 2.38	
	85,400 2.82	7,450 0.38	22,900 1.93		12,200 1.90	13,400 0.29	37,800 2.40	
	<u>87,800 2.87</u>	<u>5,520 0.21</u>	<u>17,800 2.04</u>		<u>10,400 2.19</u>	<u>34,800 1.16</u>	<u>35,500 2.47</u>	
Avg	80,100 2.65	7,450 0.32	21,000 2.00		11,900 2.04**	24,200 0.70	34,800 2.42	
Wt. Loss		0.26%	7.7%			0.25%	3.48%	
55	90,500 3.04	9,320 0.58	22,400 1.36	--	25,000 3.05	59,600 2.44	50,000 2.84	
	104,000 3.66	31,100 1.47	24,600 1.61		19,000 2.56	53,400 2.21	39,600 2.72	
	<u>99,700 3.53</u>	<u>14,200 0.62</u>	<u>12,800 1.13</u>		<u>16,200 2.85</u>	<u>51,300 1.86</u>	<u>43,100 2.78</u>	
Avg	98,100 3.41	18,200 0.89	19,900 1.37		20,100 2.82	54,800 2.17	44,200 2.79	
Wt. Loss		0.05%	17.3%			0.05%	2.76%	

** Thermoplastic failure.

TABLE VI (Continued)

Laminate No.	Flexural Strength, psi and Modulus, psi x 10 ⁶									
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	700°F after 100 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F			
56	88,100	3.13	33,500	1.70	--	70,000	2.88			
	100,500	3.58	31,400	1.42						
	92,200	3.55	31,000	1.19						
	93,600	3.42	32,000	1.44						
Avg			0.07%		25,700	3.01	2.88			
Wt. Loss			8.8%		28,800	3.08	1.87			
					22,900	3.12	2.86			
					25,800	3.07	2.54			
						0.07%	4.27%			

the previous contract year and during the course of the present program, the drying conditions required to obtain processable low volatile content prepreg causes partial advancement of the resin, and accordingly, decreases its flow. With only minimum resin flow during laminate fabrication some of the volatiles become occluded within the resin matrix which are then expelled during the postcure, resulting in blowing of the laminate.

There are several alternate ways of attempting to alleviate the postcure blowing problem such as altering the prepreg drying cycle to permit more resin flow and employ a stage cure, using longer press residence time and/or higher cure temperature, or employing an extended postcure schedule (e.g., 24 hours) at the lower temperature (e.g., 400°F). Additional laminates (Nos. 54 through 56) were fabricated using the same prepreg under three different cure conditions. Blowing during the postcure was observed for Laminate 54 which was cured at 1 hour at 750°F under 500 psi whereas no blowing was observed for Laminates 55 and 56 which were fabricated using longer cure time at 750°F or higher temperature (800°F). Apparently the longer cure times and/or higher temperature permitted the volatiles to escape while under pressure.

The test results as reported in Table VI indicate its potential as a high-temperature laminating resin.

One possible way to improve laminate properties is by examining glass fabric finishes. Since the data indicated definite potential, a brief finish evaluation was justifiable. The number of available finishes suitable for high temperature application is highly limited.

Accordingly, it was decided to evaluate a recently developed Air Force finish which has improved performance under heat aging conditions, especially against water effects. Table VII indicates comparable performance in all cases, except in the 1000°F tests, where the new AF-CA-314 finish was inferior. That flow and wetting also suffered with AF-CA-314 is indicated by lower densities and higher void content.

Laminates designated Nos. 77, 78, and 79A were fabricated under relatively mild conditions from the same prepreg (9.9% volatiles). Laminates 77 and 78, cured through 700°F, exhibited excessive blowing during the postcure. Laminate 79A, cured through 750°F, was successfully postcured. The effect of maximum postcure temperature on the performance of the composite was studied by postcuring specimens from the same laminate through 750°F and through 800°F. The 800°F postcure provides comparable performance under all test conditions, except for the 50-hour aging at 700°F in air. Apparently the higher postcure temperature of 800°F is detrimental to the aging performance of the laminate. This was also observed during the preceding program.

Laminates fabricated under mild conditions (No. 79A) and rigid conditions (No. 79B) provided essentially identical physical properties (see Table VIII).

TABLE VII
NAV-P-2 LAMINATE DATA
COMPARISON OF AF-994-AF-CA-314 AND 1581-HTS994 GLASS REINFORCED LAMINATES

Laminate Fabrication

Resin: Batch PH-6-48-S

Prepreg: Solution coated using m-cresol solution containing 18% solids; 3 dip coats, first two coats dried 15 min @ 250°F, final coat forced air dried 1 hr @ 250°F and 16 hr @ 200°C under vacuum.

Carrier: Laminates 68 and 69: AF 994-AF-CA-314

Laminates 56 and 55: 1581-HTS-994

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
68	4 x 5.8 x 6 ply	1.24	1 hr @ 800°F, 500 psi	D	--	32.6	1.58	16.0
56	4.5 x 6 x 7 ply	1.70	↓	↓	--	36.8	1.73	4.9
69	4 x 5.8 x 13 ply	1.24	4 hr @ 750°F, 500 psi	↓	--	34.0	1.57	15.6
55	4.5 x 6 x 7 ply	2.20		↓	--	36.5	1.66	8.8

* By burnout

D 22 hr @ 400°F, 23 hr @ 450°F, 23 hr @ 500°F, 20 hr @ 600°F, 4 hr each @ 700°F & 750°F in nitrogen (as test specimens).

TABLE VII (Continued)

Test Information

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶					
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F
68 (D)	86,300 3.30	15,600 0.69	20,500 1.22	5,440 1.01	59,100 2.96	37,600 2.53
Avg	83,600 2.95	23,200 1.02	28,800 1.57	12,700 1.73	61,200 2.69	30,600 2.28
	85,000 3.12	23,800 1.19	23,800 1.19	5,340 1.27	69,200 2.48	46,900 3.09
		20,900 0.97**	24,400 1.33	7,830 1.34	63,200 2.71	38,400 2.63
Wt Loss After Heat Age		0.08%	7.1%		0.09%	6.6%
56 (D)	88,100 3.13	33,500 1.70	32,300 2.46	25,700 3.01	70,000 2.88	44,000 2.99
Avg	100,500 3.58	31,400 1.42	27,500 2.30	28,800 3.08	51,500 1.87	39,600 2.87
	92,200 3.55	31,000 1.19	26,200 2.01	22,900 3.12	67,400 2.86	35,200 2.41
	93,600 3.42	32,000 1.44**	28,700 2.26	25,800 3.07	63,000 2.54	39,600 2.76
Wt Loss After Heat Age		0.07%	8.8%		0.07%	4.27%
69 (D)	77,700 3.41	13,300 1.07	15,100 1.93	4,380 1.22	-- --	-- --
Avg	87,700 3.76	9,500 0.79	19,500 1.87	5,820 1.15		
	82,700 3.58	13,100 1.04	19,000 1.96	5,100 1.18		
		12,000 0.97**	17,900 1.92			
Wt Loss After Heat Age		0.08%	5.7%			
55 (D)	90,500 3.04	9,320 0.58	22,400 1.36	25,000 3.05	59,600 2.44	50,000 2.84
Avg	104,000 3.66	31,100 1.47	24,600 1.61	19,000 2.56	53,400 2.21	39,600 2.72
	99,700 3.53	14,200 0.62	12,800 1.13	16,200 2.85	51,300 1.86	43,100 2.78
	98,100 3.41	18,200 0.89	19,900 1.37	20,100 2.82	54,800 2.17	44,200 2.79
Wt Loss After Heat Age		0.05%	17.3%		0.05%	2.76%

** Thermoplastic failure.

TABLE VIII

NAV-P-2 LAMINATE DATA
MILD CURE STUDY WITH POSTCURE EVALUATION

Laminate Fabrication

Resin: Batch PH-6-67-S

Prepreg: Solution coated using m-cresol solution containing 20% solids; 3 dip coats, first two coats dried 10-15 min @ 250°F, final coat forced air dried 1 hr @ 250°F for all laminates.

Laminate 79B prepreg dried additional 16 hr @ 200°C under vacuum.

Carrier: 1581 HTS-994

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
79B Control	6.6 x 9 x 7 ply	1.2	1 hr @ 800°F, 500 psi	E	--	32.0	1.71	9.5
77	4.5 x 6 x 7 ply	9.9	10 min @ 450°F, 200 psi & 4 hr @ 700°F, 200 psi	A & C	Badly blown ↓	--	--	--
78			10 min @ 500°F, 200 psi & 4 hr @ 700°F, 200 psi			--	--	--
79A			10 min @ 450°F, 200 psi & 4 hr @ 750°F to 800°F, 200 psi			29.7	1.73	9.9
90		10.8	10 min @ 450°F, 200 psi & 4 hr @ 750°F, 200 psi	A & B	--	33.1	1.71	8.6

TABLE VIII (Continued)

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
91	4.5 x 6 x 7 ply	10.8	10 min @ 450°F, 200 psi & 4 hr @ 800°F, 200 psi	A & B	--	31.4	1.71	10.0
92	↓	↓	10 min @ 450°F, 200 psi & 4 hr @ 750°F, 200 psi	A (as laminate)	--	32.7	1.74	7.5
93	4.5 x 6 x 14 ply	↓	↓	↓	--	31.9	1.68	11.1

* By burnout.

A 4 hr each @ 400°F & 450°F, 10 hr @ 500°F, 8 hr @ 550°F, 4 hr each @ 600°F, 650°F, 700°F, and 750°F in nitrogen.

B A + 8 hr @ 750°F in nitrogen.

C A + 2 hr @ 800°F in nitrogen.

E 20 hr @ 400°F, 22 hr @ 450°F, 22 hr @ 500°F, 6 hr @ 550°F, 14 hr @ 600°F, 3 hr @ 700°F & 4 hr @ 750°F in nitrogen.

Test Information

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶			
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F
79B (E)	116,800	3.74	35,100	2.31
Control	119,400	3.89	40,800	2.36
Avg Wt Loss after Heat Age	124,000	3.89	37,300	2.31
	120,700	3.84	37,700	2.29
	--	0.07%	4.3%	--
79A (A)	93,300	3.38+	43,700	3.08
Avg Wt Loss after Heat Age	106,600	4.15	39,300	2.59
	107,500	4.20	42,600	3.03
	102,500	3.91	41,900	2.90
	--	0.03%	7.9%	--

TABLE VIII (Continued)

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶				
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	
79A (C) Avg Wt Loss after Heat Age	89,600 3.38 95,200 3.45 103,400 4.19 96,000 3.67 --	51,400 3.69 55,100 3.62 53,250 3.66 Nil	19,200 1.93 28,800 2.16 24,000 2.02 24,000 2.04 10.6%	23,600 2.31 16,400 1.98 20,000 2.14 --	
90 (A) Avg Wt Loss after Heat Age	104,800 3.44 105,800 3.73 105,300 3.58 --	34,800 1.71 40,500 1.88 37,600 1.80** 0.05%	31,100 1.72 33,700 2.28 42,100 2.51 35,600 2.17 6.8%	25,200 2.64 20,500 2.37 22,800 2.50 --	
90 (B) Avg Wt Loss after Heat Age	98,500 3.49 100,600 3.79 99,600 3.64 --	60,600 2.52 62,600 2.36 61,600 2.44 0.68%	46,200 2.70 42,800 2.30 43,000 2.53 44,000 2.51 8.3%	13,800 2.09 20,000 2.29 16,900 2.19 --	
91 (A) Avg Wt Loss after Heat Age	100,200 3.73 90,000 3.63 95,100 3.68 --	56,900 2.56 57,300 2.46 57,100 2.51 0.08%	43,200 2.65 34,600 2.65 32,000 2.30 36,600 2.53 9.4%	8,400 2.09 25,500 2.52 17,000 2.30 --	
91 (B) Avg Wt Loss after Heat Age	95,000 3.42 83,400 3.33 89,200 3.38 --	60,100 2.75 65,400 2.39 62,800 2.56 0.84%	37,100 2.45 28,700 2.06 31,000 2.06 32,300 2.19 11.2%	16,800 2.16 24,500 2.37 20,600 2.26 --	

TABLE VIII (Continued)

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶				
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	
92 (A) (Postcured as 7 ply laminate) Avg Wt Loss after Heat Age	96,400	3.16	22,700 1.19	37,800 4.17	15,700 1.71
	113,600	3.39	25,300 1.23	30,750 4.60	15,100 2.04
	<u>103,500</u>	<u>3.35</u>	<u>24,900</u> 1.37	<u>32,320</u> 3.98	<u>29,000</u> 2.36
	104,500	3.30	24,300 1.26**	<u>33,650</u> 4.25	<u>19,900</u> 2.04
	--	--	0.17%	6.8%	--
93 (A) (Postcured as 14 ply laminate) Avg Wt Loss after Heat Age	103,400	3.68	20,700 1.76	24,700 0.86	23,900 2.83
	100,000	3.77	22,500 1.80	22,650 1.72	<u>12,600</u> 2.18++
	<u>103,500</u>	<u>3.68</u>	<u>21,600</u> 1.78**	<u>23,850</u> 1.65	<u>18,200</u> 2.50
	102,300	3.71	--	<u>23,700</u> 1.41**	--
	--	--	0.15%	7.2%	--

** Somewhat thermoplastic.

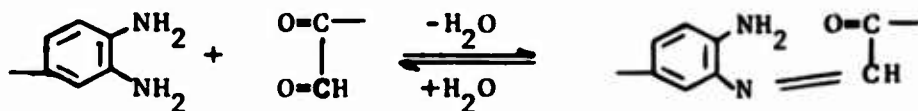
+ Edge specimens - laminate probably not trimmed sufficiently.

++ Edge specimen, narrow and porous.

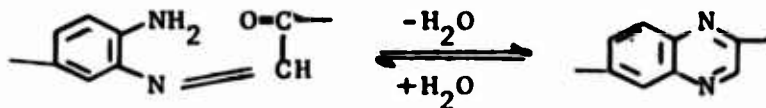
Two more laminates, Nos. 90 and 91, were fabricated in order to examine the 750°F cure as opposed to the 800°F cure. Half of the specimens were also subjected to an additional 8 hours at 750°F in nitrogen during the postcure. In essence, laminates cured to 800°F were unaffected by the extra 8-hour/750°F postcure. Laminates cured to a maximum of 750°F and exposed an extra 8 hours at 750°F postcure gave better 700°F data, after 1 and 50 hours, than laminates which were not given this additional postcure. However, contrary to what was found above, the laminates cured to 800°F were not inferior to laminates cured to a maximum of 750°F. This merely indicates that more than one factor can affect performance, and that the number of tests used during this program can only be classified as indicative. Again, the objective of this program is to indicate potential, the actual performance, as related to processing, can be determined only in an engineering data compilation program.

Laminates 92 and 93 were fabricated and postcured as total laminates. These were 7-ply and 14-ply laminates, respectively. Both laminates were cured and postcured the same as Laminate 90A. Thermoplasticity was noted after 1 hour at 700°F in both Laminates 92 and 93, while 14-ply Laminate 93 was thermoplastic after 50 hours at 700°F (see Table VIII).

Since the other laminate data were obtained by postcuring individual flexure specimens, it appears that condensation volatiles can escape more readily and the average molecular weight of the resin matrix reaches a higher level. This is based on the assumption that, as with PBI, part of the condensation may be an equilibrium process.



It is possible, but less likely than above, that the ring closure is also an equilibrium process:



While this can be determined by experiment, it is not presently considered necessary.

Based on these above data, it was decided that all future poly-quinoxaline work should be restricted to the NAV-P-2 system.

Unidirectional Composites

It was concluded that the primary objective of the program, demonstration of potential, was accomplished with NAV-P-2 and NAV-P-4 as laminating resins, on glass fabric.

At the request of Dr. P. W. Erickson and Mr. Marlin Kinna, future efforts with NAV-P-2 were focused on utilization of high-modulus reinforcements such as Thornel 40. Since the processing on such a substrate was totally unknown, it was decided to use both polyquinoxalines during the initial scanning efforts which occurred near the end of the program.

A preliminary unidirectional polyquinoxaline 7-ply Thornel 40 reinforced laminate was fabricated, and this provided encouraging test results. Although the composite had a high resin content of 43%, interesting data were observed (see Table IX). Microscopic examination of the laminates showed the excellent wetting of the Thornel fibers by the polymer.

The data in Table IX were not obtained for comparison but merely to indicate what problems are to be faced in future applications involving high-modulus fibers. However, the data do indicate that certain factors should be examined in future work. Most certainly, the very high resin contents of Laminates A, B, and C are reflected in low values at room temperature. Future efforts must optimize resin pickup so that the final composite will have resin content in the 20%-30% range. Note also that the bidirectional Laminate C was burned out after 50 hours at 700°F, while unidirectional Laminates A and B survived.

The horizontal beam test method was used to determine the interlaminar shear strength of a Thornel 40 unidirectional composite. Data at room temperature were comparable to those obtained with an epoxy, and higher than those obtained in our laboratories with other higher temperature polymers. Results were thus considered to be encouraging (see Table X).

An extra boron reinforced unidirectional composite was fabricated and processed as Laminate F (Table IX). This was tested according to the schedule in Table XI. Data are most encouraging despite indications of thermoplastic behavior (compare to 1 hour at 700°F in Table IX) of the resin and/or possible change in fiber properties with temperature.

TABLE IX

NAV-P-4 AND NAV-P-2
UNIDIRECTIONAL AND BIDIRECTIONAL THORNEL 40, RAE GRAPHITE AND BORON
(SHEATH) FIBER LAMINATE DATA (PRELIMINARY PROCESSING INFORMATION)

Laminate Fabrication

Resin: NAV-P-4 Batch PH-6-59-S Laminates A, B, C and
Batch PH-6-65-S Laminate F
NAV-P-2 Batch PH-6-67-S Laminate D

Prepreg: Laminates A, B, C, F - Teflon coated fabric was coated with 5 mil film from m-cresol solution (30-38% solids) and placed on drum, then Thornel 40 or boron (sheath) fiber was wound on drum. Subsequent fiber coatings were brush coated using 20% solids solution. Each coating was forced air dried to 250°F and final coating was forced air dried staging through 2 hr @ 380°F.

Laminate D prepreg - Graphite fibers were manually flattened and spaced on Teflon coated fabric then coated (using 20% solids solution) and dried in same manner as prepregs A, B, C, and F.

Carrier: Thornel 40 Laminates A, B & C
RAE Graphite Laminate D
Boron (sheath) Laminate F

Laminate Information

Laminate No.	Polymer & Batch	Fiber Orientation	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calc. Void Content, %
A	NAV-P-4 PH-6-59-S	Unidirectional	6 min contact @ 730°F-750°F, then 4 hr @ 750°F, 500 psi in air	F	--	43.0	1.30	3.0
B				F & H	--	42.8	1.29	5.1
C		Bidirectional alternate plies @ 90° (outside plies longitudinal in test specimen)		F & H	--	44.4	1.27	5.9

TABLE IX (Continued)

Laminate No.	Polymer & Batch	Fiber Orientation	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calc. Void Content, %
D	NAV-P-2 PH-6-67-S	Unidirectional	5 min contact @ 725°F-750°F, then 4 hr @ 750°F, 500 psi in air	G	--	32.2	1.45	--
F	NAV-P-2 PH-6-65-S	Unidirectional	5 min contact @ 725°F-750°F, then 4 hr @ 750°F, 500 psi in air	G	--	20.7	1.73	Nil

* Calculated.

F Postcure: 3-4 hr each @ 400°F, 450°F, 10-15 hr @ 500°F, 7-8 hr @ 550°F, 1-4 hr @ 600°F and 4 hr each @ 700°F & 750°F in nitrogen.

G Postcure: 4 hr each @ 400°F, 450°F, 10 hr @ 500°F, 8 hr @ 550°F, 4 hr each @ 600°F, 650°F, 700°F, & 750°F in nitrogen.

H Postcure: F + additional 1 hr @ 800°F in nitrogen.

Test Information

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶			
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F
A (F)	68,300 11.3	21,200 3.02	31,600 5.52	20,400 6.41
	76,200 12.8	18,700 2.50	31,100 5.54	16,400 5.32
	72,300 12.1	19,900 2.51	30,600 5.52	18,400 5.86
Wt. Loss	--	0.17%	15.1%	--

TABLE IX (Continued)

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶			
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F
B (F)				
	82,600	12.9	28,950	5.39
	76,200	11.7	13,900	2.48
	79,400	12.3	36,200	6.72
Avg			26,350	4.86
Wt. Loss	--	0.12%	17.0%	--
C (F)				
	44,500	8.96	Delaminated during	4,100
	46,700	8.37	heat age	0.45
	45,600	8.66		
Avg			34.6%	
Wt. Loss	--	0.08%		
C (H)				
	41,100	8.70	Delaminated during	4,260
	34,100	8.12	heat age	1.00
	37,600	8.41		
Avg			33.8%	
Wt. Loss	--	0.11%		
D (G)				
	114,200	19.6	22,200	3.65
	118,600	21.9	20,100	3.19
	103,200	18.4	22,200	3.19
	112,000	20.0	21,500	3.35
Avg			7.7%	--
Wt. Loss	--	0.67%		
F (G)				
	208,500	30.2	Burned out in	41,100
	214,100	32.8	heat age	3.93
	240,800	32.5		35,300
	221,100	31.8		38,200
Avg				2.56
Wt. Loss	--	0.14%		3.24

Laminate Fabrication

Resin: Batch PH-6-59-S

Prepreg: Teflon coated with m-cresol solution containing ~31% solids (based upon final polymer) was placed on a drum and Thornel 40 fiber wound around the drum. The resulting prepreg was dried in a forced air oven while on the drum followed by brush coating with additional solution (20% solids) twice, drying in a forced air oven to 250°F after each coat.

Carrier: Thornel 40

Cure

Conditions: 6 min contact time @ 730°F, then 4 hr @ 750°F under 500 psi in air

Postcure: 3 hr each @ 400°F & 450°F, 15 hr @ 500°F, 8 hr @ 550°F, & 4 hr each @ 600°F, 700°F, & 750°F in nitrogen for laminate B-1 and an additional 1 hr @ 800°F for laminate B-2

Laminate Information

Calculated Resin Content: 43%

Calculated Void Content: 3.0%

Bulk Density: 1.30 g/cc

Dimensions: 4 in. x 4 in. x 7 ply

Type: Unidirectional

Test Information

Laminate No. & (Postcure)	Shear Strength - Horizontal Beam Method				
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F
B (F)	3080	1030	*	788	1250
	3020	1360	655	575	1050
	3090	1260	961	643	1190
	Avg 3060	1220	808	669	1160
B (H)	3030	1470	959	855	882
	2870	1290	886	842	519
	2930	1420	886	324	824
	Avg 2940	1390	910	680	742

* Failed in handling

TABLE XI

**NAV-P-2 UNIDIRECTIONAL BORON LAMINATE
TESTED AT TEMPERATURE AFTER 3-MINUTE EXPOSURE**

Test Temp, °F	Flexural Strength, psi*	Modulus, psi x 10 ⁶
RT	253,000	42.3
270	197,000	36.2
350	200,600	37.5
420	180,200	37.0
600	220,800	24.2
700	241,500	12.1

* Average of duplicates.

Structurally Modified Polyquinoxalines

The slight tendencies toward thermoplasticity in NAV-P-2 and NAV-P-4 could be detrimental because of possible creep and because of definite limitation on upper temperature utility. At the very end of the program, the first structural modification of NAV-P-2 was successfully carried out; a copolymer was synthesized from 3,3'-diaminobenzidine and a mixture of 75 mole-% of 4,4'-diphenyletherbisglyoxal and 25 mole-% of *p*-phenylene glyoxal. The structure of the resulting polymer is unknown, but it is suspected that a random block copolymer resulted. Partial removal of the ether linkage and substitution by the *p*-phenylene moiety should increase crystallinity and stiffness. The results are shown in Table XII along with typical, good data of an unmodified NAV-P-2. A code name of NAV-P-5 was assigned to the modified polymer. The most significant data are those at 1000°F. Note that the copolymer has a modulus of 3.23×10^6 psi as compared to 2.19×10^6 psi for the unmodified structure; also, the flexural strength is almost double. Aging data after 50 hours at 700°F and 200 hours at 600°F, in air, were most gratifying.

Adhesive Studies

Tensile shear specimens were fabricated from tape prepared from the *m*-cresol solution formulated with 50-phr of amorphous boron. The relatively poor test data reported in Table XIII are again attributed to the limited flow of the resin. Bonds prepared during the previous contract year provided average tensile shear strengths as high as 3520 psi at room temperature and 2200 psi at 700°F after 50 hours at 700°F in air. Lower molecular weight NAV-P-4 will be prepared and evaluated.

TABLE XII

NAV-P-5 LAMINATE DATA (COPOLYMER) VS NAV-P-2 LAMINATE DATA

Laminate Fabrication

Resin: Batch RR-2110-17 Laminate 107 (copolymer)
Batch PH-6-67-S Laminate 90

Prepreg: Laminate 107 - solution coated using m-cresol solution containing 12% solids, 7 dip coats, forced air dried 10 min @ 250°F between coats with final 1 hr @ 250°F.

Laminate 90 - solution coated using m-cresol solution containing 20% solids, 3 dip coats, forced air dried 10-15 min @ 250°F between coats with final 1 hr @ 250°F.

Carrier: 1581 HTS-994

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
107	4.5 x 6 x 7 ply	4.85	10 min @ 550°F 200 psi and 4 hr @ 750°F 200 psi	B as specimens ↓	27.8	1.77	9.2
90	4.5 x 6 x 7 ply	10.8	10 min @ 450°F 200 psi and 4 hr @ 750°F 200 psi		33.1	1.71	8.6

* By burnout

B 4 hr each at 400°F & 450°F, 10 hr @ 500°F, 8 hr at 550°F, 4 hr each at 600°F, 650°F & 700°F, and 12 hr @ 750°F in nitrogen.

TABLE XII (Continued)

Test Information

Laminate No.	Flexural Strength, psi and Modulus, psi x 10 ⁶						
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	1000°F after 1 hr @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F
107 Avg Wt. Loss	105,100	53,800	51,200	32,600	14,200	70,200	59,200
	3.43	2.48	3.05	3.23	2.10	2.96	3.26
	106,900	44,000	49,900	30,900	11,200	79,800	68,400
	3.35	2.17	2.34	3.23	1.83	3.27	3.70
	104,900	54,600	48,700	31,750	12,700	75,000	45,600
90 Avg	3.57	2.83	3.10	3.23	1.97	3.09	3.10
	105,600	50,800	49,900	31,750	12,700	75,000	57,700
	3.45	0.05%	5.82%	3.23	1.97	3.09	3.35
						0.03%	4.66%
90 Avg	98,500	60,600	46,200	13,800	--	--	--
	3.49	2.52	2.70	2.09	--	--	--
	100,600	62,600	42,800	20,000	--	--	--
	3.79	2.36	2.30	2.29	--	--	--
	99,600	61,600	44,000	16,900	--	--	--
90 Avg	3.64	0.68%	8.3%	2.19	--	--	--

TABLE XIII
TENSILE SHEAR STRENGTH OF NAV-P-4
PRELIMINARY PROCESSING DATA

<u>Adhesive</u>		Batch PH-6-59-S			
Resin:		50-phr amorphous boron			
Filler:		112-A-1100, tape prepared from <u>m</u> -cresol solution and dried to volatile content of 28.6%			
Carrier:		Panel A, 1 hr each @ 525°, 625°, 725°, and 850°F under 100 psi in nitrogen Panel C, 1 hr each @ 630°, 730°F, and 850°F under 200 psi in nitrogen			
Cure:					
Postcure:	None				
<u>Substrate</u>					
Metal:		PH 17-7 stainless steel			
Surface Preparation:		Conventional phosphate etch			
Primer:		Same resin			
<u>Test Information</u>					
Panel No.	Tensile Shear Strength, psi				
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F
A	2400 2100 1900 <u>2100</u>	836 982 <u>1129</u> 982	Burned out	876 736 <u>672</u> 761	--
Avg					
C	2020 1880 1690 <u>1860</u>	--	Burned out	1000 950 <u>1090</u> 1010	1490 1770 <u>1450</u> 1570
Avg					

The test data given in Table XIV indicated comparable adhesion between stainless steel and titanium. Unfortunately, the tape was advanced too far, and this resulted in limited flow and poor wetting of the substrate.

The data in Table XV were obtained with the half ether polyquinoxaline. Results were extremely encouraging because of the improvement over previous data with the diether. Particularly interesting are the aging data after 200 hours at 600°F and 50 hours at 700°F, all in air because of excellent strength retention and an apparent postcuring effect despite the rigorous cure conditions.

Compatibility With High Temperature Stable Explosives

A sample of NAV-P-4 (PH-6-57AP, $\eta_{inh} = 1.68$) and NAV-P-10 (P-6-6-62P, $\eta_{inh} = 1.71$) was submitted for evaluation with ONT (octanitroterphenyl) and HNS (hexanitrostilbene).

The data were determined and reported by Mr. H. T. Simmons, Sr, of NOL, to Dr. P. W. Erickson, in a memorandum on 31 January 1968. Both were compatible at 260°C for 2 hours or longer. It appeared that NAV-P-10 was somewhat more stable; this is the phenyl substituted polyquinoxaline. See Table XVI.

Initial Evaluation for Fiber Potential

Fibers were prepared by a "hand" operation from small samples of NAV-P-2 and NAV-P-4 in *m*-cresol. Information received from Mr. B. S. Sprague, Manager of Materials Science Research of Celanese Research Company. Mr. Sprague's comments included, "It appears that both materials can be formed into fibers with interesting high temperature properties with the half ether PQ perhaps being somewhat more interesting than the diether. The data are shown in Table XVII.

POLYPHENYLQUINOXALINES

The polyphenylquinoxalines are synthesized by condensation of a bisbenzil and a bis-*o*-diamine:

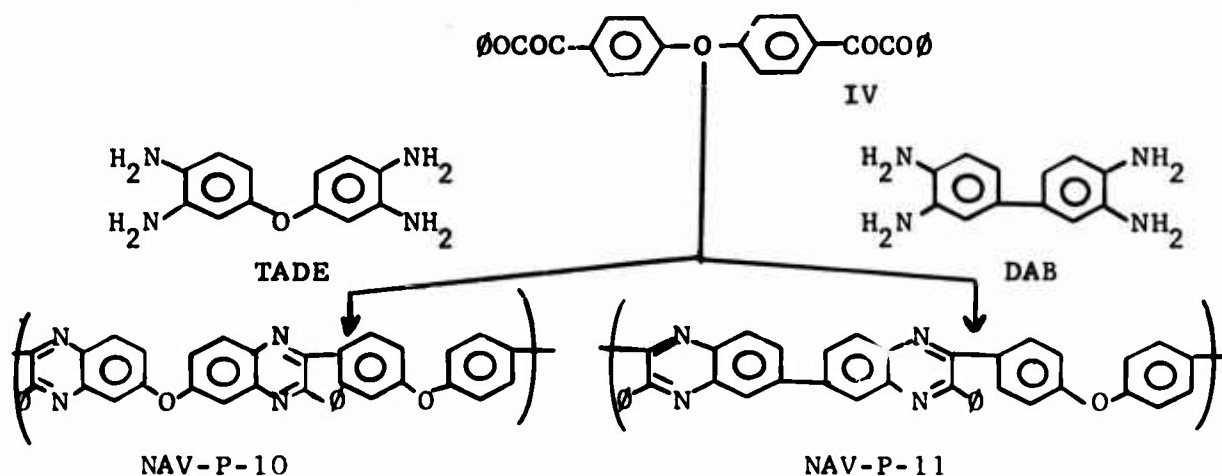


TABLE XIV

NAV-P-4 TENSILE SHEAR DATA
PRELIMINARY PROCESSING DATA

Adhesive

Resin: Batch PH-6-59-S
 Filler: 50 phr Amorphous boron
 Carrier: 112 A-1100; tape prepared from m-cresol solution formulated with boron, dried to following volatile content:
 Panel No. O and Q, 7.5%
 Panel No. Y and AA, 3.8%

Cure

Conditions: 1 hr each @ 650°F, 750°F & 850°F under 200 psi in nitrogen

Postcure: None

Substrate

Metal: Panel No. O and Y, PH-17-7 stainless steel
 Panel No. Q and AA, 8-1-1 Titanium

Surface

Preparation: Conventional phosphate etch

Primer: Same resin

Test Information

Panel No.	Tensile Shear Strength, psi			
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F
O	2310	1920	1470	1130
	2570	1500	260	1140
	<u>2040</u>	<u>1960</u>	<u>460</u>	<u>1270</u>
Avg	2310	1790	730	1180
Q	1570	1660	1913	1290
	1700	1520	684	1200
	<u>1520</u>	<u>1790</u>	<u>784</u>	<u>990</u>
Avg	1600	1660	1130	1160
Y	2230	1720	755	1170
	1850	1620	1870	1240
	<u>2750</u>	<u>1970</u>	<u>1930</u>	<u>980</u>
Avg	2280	1770	1520	1130
AA	1670	1810	820	924
	1380	1650	1230	1100
	<u>1820</u>	<u>1400</u>	<u>1340</u>	<u>1120</u>
Avg	1620	1620	1130	1050

TABLE XV

NAV-P-2 TENSILE SHEAR DATA
PRELIMINARY PROCESSING DATA

Adhesive

Resin: Batch PH-6-48-S

Filler:

Panel No. E, G, and K; 50 phr amorphous boron
Panel No. I and M; 30 phr amorphous boron

Carrier: 112 A-1100; tape prepared from m-cresol PQ solution formulated with boron,
dried to the following volatile content:

<u>Panel No.</u>	<u>E and G</u>	<u>I</u>	<u>K</u>	<u>M</u>
Volatile Content, %	16.1	15.3	11.3	9.6

Cure Conditions: 1 hr each @ 650°F, 750°F, & 850°F under 200 psi in nitrogen

Postcure: None

Substrate

Metal: PH 17-7 stainless steel

Surface Preparation: Conventional phosphate etch

Primer: Same resin

Test Information

Panel No.	Tensile Shear Strength, psi				
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F
E	3630 3040 3490 Avg	1620 1480 1780 1630	1904 980 1492 1460	1030 1280 1340 1220	--
G	3660 3230 3150 Avg	--	--	1444 1308 1456 1400	3020 2940 2830 2930
					2500 2120 2220 2280

TABLE XV (Continued)

Panel No.	Tensile Shear Strength, psi					
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 1 hr @ 600°F	600°F after 200 hr @ 600°F
I	3390	2480	2650	--	--	--
	2840	1780	2000			
	2690	1750	2720			
	<u>2970</u>	<u>2000</u>	<u>2460</u>			
Avg						
K	3640	1680	2550	1270		
	3070	2080	2560	<u>1380</u>		
	3040	<u>1860</u>	<u>2500</u>	<u>1325</u>		
	<u>3250</u>	<u>1870</u>	<u>2540</u>			
Avg						
M	2740	2560	2660	1610		
	2850	1930	2150	1350		
	2920	1670	2510	<u>940</u>		
	<u>2840</u>	<u>2050</u>	<u>2440</u>	<u>1300</u>		
Avg						

TABLE XVI

STABILITY OF POLYQUINOXALINES WITH
HIGH TEMPERATURE STABLE EXPLOSIVES⁽¹⁾

Sample	Mixture %	Surge (20")	2 hr Period
ONT X641	100	0.15	0.30
ONT X641 + PH-6-57AP	80/20	0.58	0.26
ONT X641 + PH-6-6-62P	80/20	0.36	0.23
HNSII X626	100	0.33	0.20
HNSII X626 + PH-6-57-AP	80/20	1.12	0.63
HNSII X626 + PH-6-57-AP	80/20	0.57	0.56

(1) See letter of F. R. Barnet, 234:PWE:hz.

NOTE: "No initial surge was detected as is generally the case with polymers where volatiles and trapped solvent leave the system no matter how long they were cured or aged. Both polymers mixed with the two explosives did not appear to interact or decompose at 260°C for the 2 hour period or longer. These polymers are compatible and highly stable when mixed with the two explosives at 260°C."

TABLE XVII
INITIAL FIBER EVALUATION
NAV-P-2 AND NAV-P-4 POLYMERS

	Tensile Properties (60% strain rate, 3-1/3" gauge)			
	Denier	Elongation %	Tenacity g/d	Modulus g/d
<u>NAV-P-2</u>				
1. Drawn 275°C (Uncured)	44.7	0.99	0.64	72.4
	42.0	1.50	0.48	33.3
	57.2	2.40	0.72	40.6
	74.6	2.31	0.55	27.5
	57.6	1.44	0.56	49.3
2. Drawn 300°C-325°C (Cured 220°C)	28.9	7.96	2.52	74.9
	28.9	9.16	1.31	39.3
	40.4	3.15	2.13	88.2
	41.8	6.12	3.20	91.6
	37.8	3.00	2.17	95.4
(60% strain rate, 1/2" gauge)				
3. Drawn 325°C (Cured 220°C)	73.1	22.2	1.74	22.0
	73.1	19.0	2.61	37.5
4. Drawn 325°C (Cured 220°C) Tested at 400°C	73.1	23.5	0.8	20.1
5. Drawn 325°C (Cured 220°C) Aged 100 hr at 320°C Tested at RT	73.1	4.44	0.8	19.4
<u>NAV-P-4</u>				
(60% strain rate, 2" gauge)				
1. Drawn 275°C-300°C (Cured 300°C)	32.6	20.0	1.78	26.7
	74.6	21.3	1.52	33.3
	29.3	11.8	1.24	27.7
(60% strain rate, 1" gauge)				
2. Drawn 275°C to 300°C (Cured 300°C) Tested at 400°C	22.5	8.3	0.34	--
	50.2	21.7	0.14	--
	68.0	13.4	0.09	--
	55.8	16.0	0.27	--
	60.3	19.4	0.13	--

TABLE XVII (Continued)

	Tensile Properties (60% strain rate 1-1/2" gauge)			
	Denier	Elongation	Tenacity	Modulus
<u>NAV-P-4</u>				
3. Drawn 275°C to 300°C	52.3	2.5	0.47	25.2
(Cured 300°C)	46.1	1.13	0.40	37.3
Aged 100 hr at 320°C	60.7	1.31	0.28	21.8
Tested at RT	76.0	2.87	1.31	46.0

NOTES: A. Fibers were manually prepared from a solution of the polymer, in m-cresol (14.3% solids by weight), as supplied by the Whittaker Corporation. Coagulation of the fiber was accomplished with a mixture of 50/50 ethanol/water by volume. Fibers were leached for 3 days with isopropanol. Optimum fibers preparation conditions were not established. Note: each fiber is individually prepared and the properties of each fiber should be judged separately.

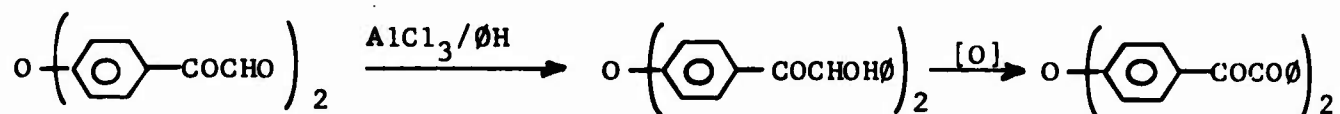
The x-ray diagrams of the above fibers showed the fiber to be generally amorphous and unoriented.

B. Fibers were prepared in the same manner as A. The m-cresol solution supplied by the Whittaker Corporation contained 16.6% solids. The fibers so formed appeared to be further from optimum conditions than A.

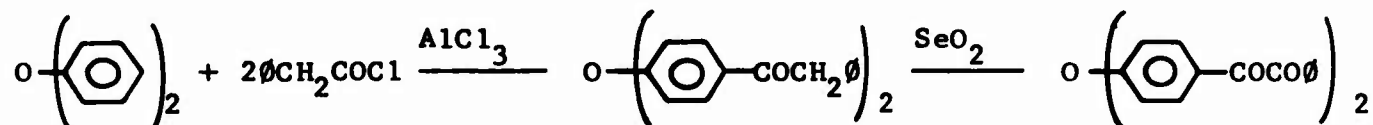
The x-ray diagram showed the original fiber before aging to be generally amorphous and slightly oriented.

The advantageous effect of improved oxidative stability when the pyrazine hydrogen of the quinoxaline ring is substituted with a phenyl group has previously been fully described.(2)

The preparation of the dibenzil during the previous contract year was successfully accomplished in good yield, as shown in the following equation for the preparation of 4,4'-oxydibenzil.

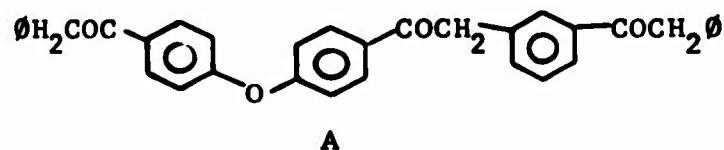


However, this route involved the use of a relatively expensive reactant, the diglyoxal, making the preparation of the dibenzil an expensive and time-consuming operation. A number of less costly and more convenient routes were considered for the synthesis of the dibenzil. The most promising route appeared to be that of Ogliaruso,(3) which concerned the acylation of diphenyl ether with phenylacetyl chloride followed by oxidizing the intermediate didesoxybenzoin to the desired dibenzil, as indicated below.



Following the procedure of Ogliaruso, the acylation of diphenyl ether was performed in carbon disulfide, using aluminum chloride to provide a quantitative yield of crude product melting at 154°-158°C (literature reports mp 169°-170°C for phenylacetylphenyl ether).

A study on the synthesis of ODB by the following route was carried out and is summarized in Table XVIII. The initial preparation (Reaction 1 in table) of *p,p'*-di(phenylacetylphenyl) ether was by the above known procedure.(3) Modification of the reaction conditions (Reactions 2 and 3 in table) also failed to provide reasonably pure *p,p'*-di(phenylacetylphenyl) ether. Apparently excess acylation occurred to form compound A when an



excess of acylating agent and catalyst were used. The solubility characteristics of the contaminant parallels those of the desired product,

(2) P. M. Hergenrother and H. H. Levine, J. Polymer Sci., **A-1**, 5, 1453 (1967).

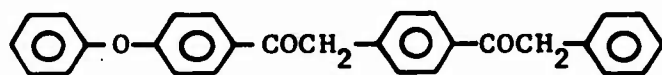
(3) M. A. Ogliaruso et al., J. Org. Chem., **28**, 2725 (1963).

TABLE XVIII

PREPARATION OF P,P'-DI(PHENYLACETYLPHENYL) ETHER

Reaction	Reaction Stoichiometric in moles			Solvent	Addition Temp, °C	Crude Product		Purified Product	
	Diphenyl Ether	Phenylacetyl Chloride	Aluminum Chloride			Yield, %	mp, °C	Yield, %	mp, °C
1	0.1	0.24	0.24	Carbon Disulfide (100 ml)	5	100	154-158	--	--
2	0.1	0.3	0.3	Carbon Disulfide (100 ml)	25	125	130-134	--	--
3	0.1	0.3	0.3	Tetrachloroethane (100 ml)	25	83	148-152	--	--
4	0.12	0.24	0.24	Carbon Disulfide (100 ml)	25	99	170-173	80	174-175.5
5	1.0	2.00	2.00	Carbon Disulfide (1 l)	25	85	165-169	68	170-172

thereby making purification by recrystallization impractical. However, a quantitative yield of *p,p'*-di(phenylacetylphenyl) ether was obtained (Reaction 4 in table) when a theoretical amount of catalyst and acylation agent were used. It is readily apparent that another compound which can be formed in this reaction is *p*-phenoxyphenyl-*p'*-phenylacetylbenzyl ketone (B). However, this compound can be oxidized to a reactant which would



B

yield polymer without disrupting the stoichiometry. The effect small amounts of this material may impart upon the final properties of the polymer are purely speculative.

The preparation of the ODB intermediate, *p,p'*-di(phenylacetylphenyl) ether, using phenacyl halide instead of phenylacetyl chloride was considered but deemed undesirable at this time due to the lacrymatory effect of phenacyl halides.

An initial large scale synthesis (1770 g) of *p,p'*-di(phenylacetylphenyl) ether provided a 67% yield (1152 g) of pure product.

Oxidation of *p,p'*-di(phenylacetylphenyl) ether with selenium dioxide was accomplished in an acetic anhydride-acetic acid mixture after first failing in aqueous dioxane. Problems initially encountered in achieving complete oxidation were overcome by employing a long reflux period. A two-mole oxidation (790 g) provided a 66% yield (557 g) of polymer grade ODB.

Polymer

Two preliminary small-scale (0.10 mole) polymerizations were conducted. The diether polyphenylquinoxaline (NAV-P-10) was prepared in *m*-cresol and exhibited an inherent viscosity (0.5% H₂SO₄ at 25°C) of 0.66 after heating to 130°C for 45 minutes and 0.69 after heating to 200°C for 2 hours. Final polymer having an inherent viscosity of 1.57 was obtained after advancing the isolated prepolymer under nitrogen for 1 hour at 400°C. A *m*-cresol solution containing 21% solids was conveniently prepared and used in application work.

The half ether PPQ (NAV-P-11) was also prepared in *m*-cresol and exhibited an inherent viscosity of 1.91 as the final polymer. A portion of the *m*-cresol solution was doctored onto a glass plate and dried by heating to 200°C under nitrogen during 6 hours to provide a clear lemon-yellow film which exhibited excellent toughness and flexibility. Additional curing was performed at 300°C under nitrogen for 1 hour. Table XIX shows the properties of this film.

The data provided the first clue that the polymers would present a problem due to thermoplasticity.

TABLE XIX

NAV-P-11 FILM, BATCH PH6-61-S

Test Temp, °C	Ultimate Tensile Strength, psi	Modulus, psi x 10 ⁵	% Elongation
RT	14,300	3.24	8.1
350	10,900	2.68	25.0
500	6,160	2.22	--
600	No Load	--	--

Fabrication of the first laminate showed that the polymer provided excellent room temperature values but that thermoplasticity was beyond a reasonable, tolerable degree as illustrated in Table XX.

More laminates were fabricated and tested. The data given in Table XXI indicated thermoplasticity again, but there was good strength retention at 700°F and encouraging numbers after 200 hours at 600°F.

NAV-P-11 was used to prepare 7-ply laminates. The poor data are attributed to the limited flow obtained during laminate fabrication. This is further indicated by the high void content of the cured laminate despite the very low volatiles content (1.5%) of the prepreg (see Table XXII). The solution used to make the prepreg had a resin concentration of only 7.7%, because the very high molecular weight of the polymer gave the solution a very high viscosity. Consequently, during laminate cure, resin flow was marginal even at 800°F at 500 psi. Future resins will have to be prepared with lower inherent viscosities, although this will have to be re-determined because of the future phenyl-substituted polymers envisioned.

It is evident that the phenyl substitution in the polyquinoxaline structure caused a decided increase in thermoplasticity, marginally present in the nonsubstituted backbone. The phenyl-substituted polymers synthesized had the diether and half ether structures because the required monomers were available and provided the most rapid evaluation of the oxidation behavior of the polymer. In view of this thermoplastic behavior, it would be wise to discontinue laminate fabrication with the same polymer structure. Accordingly, new polyphenylquinoxalines will be synthesized in which the structures will be modified in an attempt to increase glass transition temperature (T_g) and rigidity. The synthesis of new bis- α -diketones will be attempted. Upon synthesis, these will then be reacted with 3,3'-diaminobenzidine to provide new polyphenylquinoxaline structures. Thus,

TABLE XX

Laminate Fabrication

NAV-P-10 LAMINATE DATA

PRELIMINARY PROCESSING STUDY

Resin: Batch PH-6-62-S

Prepreg: Solution coated using m-cresol solution containing 21% solids; 2 brush coats, first coat forced air dried 10-15 min @ 250°F, second coat forced air dried 1 hr @ 250°F followed by 2 hr @ 330°-385°F under vacuum.

Carrier: 1581 HTS-994

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin Content, %	Bulk Density, g/cc	Calculated Void Content, %
64	4 x 6 x 7 ply ↓	2.18	1 hr @ 750°F, 50 psi	A	Blowing	--	--	--
65		2.45	4 hr @ 750°F, 50 psi	A	--	33.7	1.64	11.8
66		2.45	2 hr @ 800°F, 50 psi	A	--	30.6	1.86	2.1

A 4 hr each @ 400°F & 450°F, 13 hr @ 500°F, 7 hr @ 550°F, 4 hr each @ 600°F, 700°F & 750°F.

Test Information

Laminate No.	Flexural Strength, psi and Modulus, psi x 10 ⁶				
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 200 hr @ 600°F
65	110,800 3.45	4,840 0.49 4,640 0.41 4,740 0.45 0.27%	11,900 1.25 10,400 1.24 11,150 1.25 5.5%	3,350 0.95 3,520 0.72 3,440 0.84	22,500 1.54 19,200 1.43 20,850 1.48 3.2%
66	118,300 3.97	7,920 0.93 8,450 1.04 8,180 0.98 0.23%	19,600 1.89 17,700 1.80 18,650 1.84 5.2%	9,980 2.06 10,720 2.03 10,350 2.04	36,600 2.60 33,500 2.86 35,050 2.73 3.5%
Wt. Loss					

TABLE XXI
NAV-P-10 LAMINATE DATA

Laminate Fabrication

Resin: Batch PH-6-69-BS

Prepreg: Solution coated using m-cresol solution containing 20% solids; 3 dip coats, forced air dried 10 min after first and second coat and 60 min @ 250°F after third coat. Then dried 2 hr @ 330°-385°F under vacuum.

Carrier: 1581 HTS-994

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
84	4.5 x 6 x 7 ply	2.0	2 hr @ 800°F, 200 psi ↓	A	--	26.9	1.79	4.8
85	4.5 x 6 x 7 ply	2.0		A	--	27.2	1.77	9.2

* By burnout.

A 4 hr each @ 400°F & 450°F, 10 hr @ 500°F, 8 hr @ 550°F, 4 hr each @ 600°F, 650°F, 700°F, & 750°F in nitrogen.

Test Information

Laminate No.	Flexural Strength, psi and Modulus, psi x 10 ⁶					
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 200 hr @ 600°F	
84	111,300 3.68	12,900 1.13	21,800 2.17	11,140 2.04	33,740 2.79	
	121,700 3.77	19,600 1.59	19,600 1.59	8,960 1.86	31,000 2.58	
	109,700 3.83	14,500 1.64	16,800 1.86	6,000 1.69	25,550 2.48	
Avg	114,700 3.76	13,700 1.38**	19,400 1.87**	8,700 1.86	30,100 2.61	
Wt. Loss	--	0.06%	7.35%	--	5.93%	

TABLE XXI (Continued)

Laminate No.	Flexural Strength, psi and Modulus, psi x 10 ⁶									
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	600°F after 200 hr @ 600°F					
85	107,900	4.06	10,300	1.03	14,250	1.72+	6,680	1.69	8,490	2.35+
	114,000	3.73	10,600	1.24	17,500	1.66	8,440	1.97	26,400	2.17
	114,300	3.76	13,200	1.62	7,500	1.64+	6,780	1.84	26,100	2.20
	112,000	3.85	11,400	1.30**	13,000	1.67**	7,380	1.83	20,330	2.24
Avg				0.06%		8.70%	--	--		--
Wt. Loss		--								

** Thermoplastic failure

+ Edge specimen

++ Delaminated end

TABLE XXII
NAV-P-11 LAMINATE DATA

Laminate Fabrication

Resin: Batch PH-6-69-CS
Prepreg: Solution coated using m-cresol solution containing 7.7% solids; 7 dip coats, forced air dried @ 250°F for 10-15 minu each coat. Then dried 2 hr 330°-385°F under vacuum.
Carrier: 1581 HTS-994

Laminate Information

Laminate No.	Size, in.	Prepreg Volatile Content, %	Cure Conditions	Postcure Schedule	Postcure Comment	Resin* Content, %	Bulk Density, g/cc	Calculated Void Content, %
82	4.5 x 6 x 7 ply ↓	1.5	2 hr @ 800°F, 500 psi ↓	A & B ↓	--	31.2	1.59	16.3
83		1.5			--	32.4	1.59	15.4

* By burnout.

A 4 hr each @ 400°F & 450°F, 10 hr @ 500°F, 8 hr @ 550°F, 4 hr each @ 600°F, 650°F, 700°F, & 750°F in nitrogen.
B A + 8 hr @ 750°F in nitrogen.

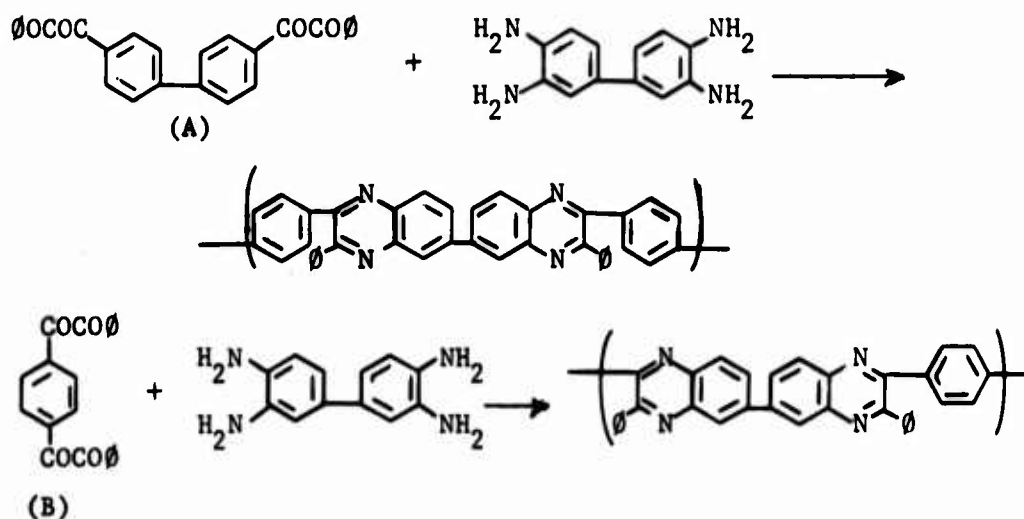
Test Information

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶			
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F
82 (A)	48,100 3.11 55,500 2.98 47,600 3.07 50,400 3.05	12,400 0.43 12,800 0.42 12,600 0.43**	4,360 0.67 4,510 0.65 4,680 0.70 4,520 0.67**	9,300 1.65 8,970 1.77 9,140 1.71
Wt. Loss	--	0.06%	10.2%	--

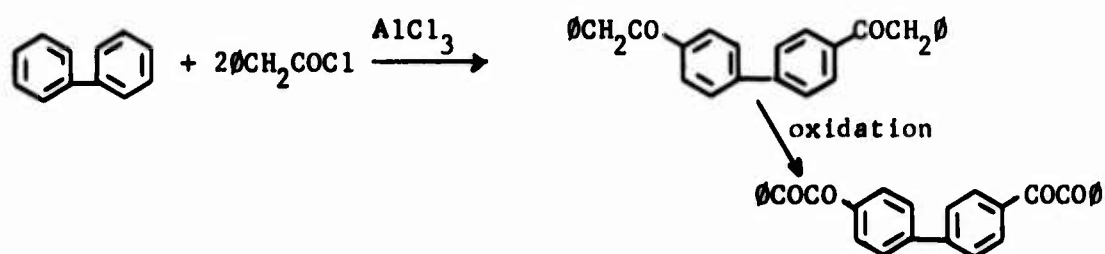
TABLE XXII (Continued)

Laminate No. & (Postcure)	Flexural Strength, psi and Modulus, psi x 10 ⁶				
	RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F	
82 (B)	55,400 3.08	14,500 0.43	2,760 0.34	10,300	2.00
	47,800 3.10	13,900 0.42	2,630 0.36	10,000	1.86
	48,400 3.20	14,200 0.43**	2,550 0.25	10,150	1.93
Wt. Loss	50,500 3.13	0.08%	2,650 0.32**	--	--
83 (A)	51,200 2.94	13,400 0.33	4,430 0.73	9,420	1.61
	57,800 2.99	11,700 0.32	5,080 0.59	10,680	1.67
	60,500 2.93	12,600 0.33**	4,950 0.76	10,050	1.64
Wt. Loss	56,500 2.95	0.04%	4,820 0.69**	--	--
83 (B)	59,400 3.13	12,400 0.37	3,950 0.60	11,000	1.95
	60,500 3.04	13,100 0.38	3,650 0.60	10,400	1.69
	62,200 3.06	12,800 0.38**	4,200 0.62	10,700	1.82
Wt. Loss	60,700 3.08	0.08%	3,930 0.61**	--	--

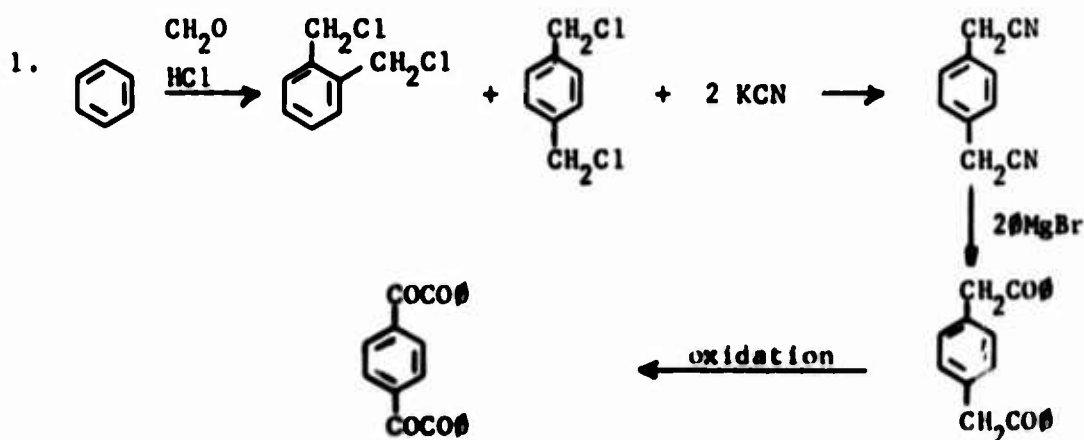
** Thermoplastic failure.

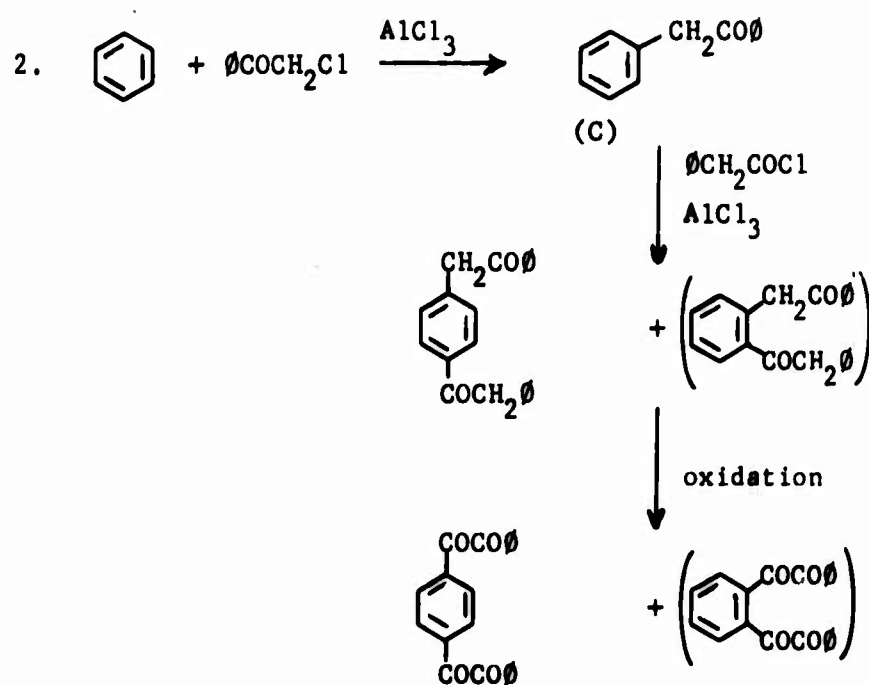


The synthesis of (A) above should be relatively simple and analogous to that used for the diphenylether analogue,



Synthesis of (B) is more difficult since use of ClCH_2COCl will introduce a carbonyl linkage into the benzene ring, causing deactivation which will probably make the second substitution extremely difficult. The following routes are under consideration:





Compound (C) is not deactivated because the ring is substituted by a $-\text{CH}_2$ group rather than a $-\text{CO}-$ group.

Tensile shear data given in Table XXIII merely reflects the previous laminate results; i.e., excellent room temperature properties but thermoplastic failure at elevated temperatures.

POLYBENZOTHAZOLES

Polybenzothiazoles research involved limited synthetic work on two polymers, an AA-BB type from the reaction of 3,3'-dimercaptobenzidine dihydrochloride with diphenyl isophthalate and an A-B type from the self polycondensation of 3-amino-4-mercaptobenzamide, as shown in the following equations:

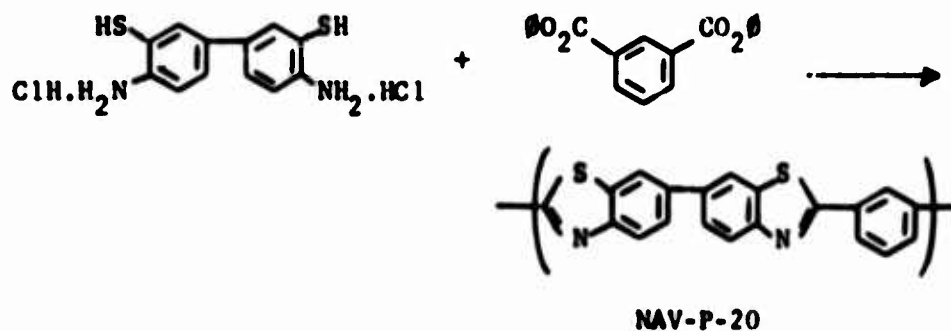


TABLE XXIII

NAV-P-10 TENSILE SHEAR DATA
PRELIMINARY PROCESSING STUDY

Adhesive
Resin: Batch PH-6-62-S
Filler: 50 phr amorphous boron
Carrier: 112-A-1100; tape prepared from m-cresol solution formulated with boron, dried to volatile content of 4.0%
Cure
Conditions: Contact time in hot press until 650°F attained then under 50 psi for 1 hr each @ 650°F, 750°F, & 800°F in nitrogen
Postcure: Where indicated: 4 hr each @ 400°F & 450°F, 13 hr @ 500°F, 7 hr @ 550°F, 4 hr each @ 600°F, 700°F, & 750°F, and 1 hr @ 800°F

Substrate
Metal: Panel No. S and U, PH 17-7 stainless steel
Panel No. W, 8-1-1 Titanium
Surface
Preparation: Conventional phosphate etch
Primer: Same resin

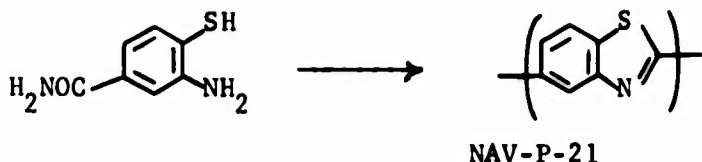
Test Information

Panel No.	Postcure	Tensile Shear Strength, psi			
		RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F
S	No	3200 3570 3280 3350	260 254 332 282	526 626 518 557	142* 534 460 497
Avg					

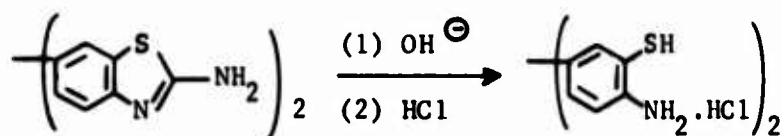
* Single specimen.

TABLE XXIII (Continued)

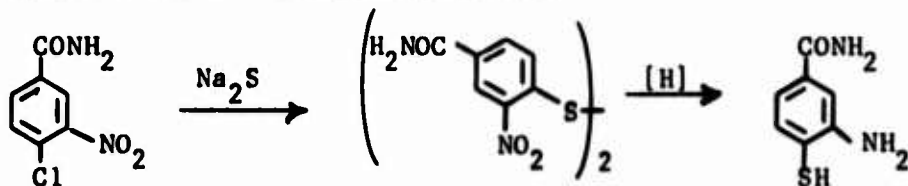
Panel No.	Postcure	Tensile Shear Strength, psi			
		RT	700°F after 1 hr @ 700°F	700°F after 50 hr @ 700°F	1000°F after 10 min @ 1000°F
U	Yes	3880 3760 3720 3790	1680 470 920 1020	2040 830 640 1170	1310 332 572 738
Avg					--
W	Yes	3640 3690 3940 3760	650 720 500 643	980 980 1120 1030	974 916 600 821
Avg					--



3,3'-Dimercaptobenzidinedihydrochloride was prepared from 6,6'-bis(2-aminobenzothiazole) as shown in the following equation after high-polymer formation failed using commercially available monomer.



Following the procedure outlined in the 1966 Final Report, (1) 3-nitro-4-chlorobenzamide was reacted with sodium sulfide to yield bis(2-nitro-4-carbamylphenyl) disulfide which was hydrogenated to provide a quantitative yield of crude 3-amino-4-mercaptobenzamide. Recrystallization afforded polymer grade 3-amino-4-mercaptobenzamide.



After several unsuccessful attempts to synthesize high molecular weight polybenzothiazole from purified commercially available monomer, polymer which exhibited an η_{inh} (0.5% H_2SO_4) of 0.69 was successfully obtained from prepolymer synthesized from monomer prepared by Narmco and diphenyl isophthalate in N,N-diethylaniline. Polymer having an inherent viscosity of 1.07 was also prepared from DMBdiHCl and isophthamide in polyphosphoric acid. These two preliminary experiments demonstrated that relatively high molecular weight polymer can be prepared from this DMBdiHCl.

Therefore, prepolymer (250 g) was prepared from the reaction of monomer and diphenyl isophthalate in N,N-diethylaniline for evaluation in application work. Although the prepolymer exhibited a polymer fusion temperature (PFT) of 220°-230°C, poor wetting of the glass cloth was observed when laminate fabrication was attempted. Since 14-ply laminates were fabricated during the previous contract year from similar prepolymer, the newly synthesized prepolymer was characterized in an attempt to discover the reason for the unusual behavior. The prepolymer exhibited an inherent viscosity of 0.13 and a volatile content of 9%, which indicated that the prepolymer had been advanced too far to exhibit good flow properties.

3-Nitro-4-mercaptobenzamide was polymerized under nitrogen in commercial grade polyphosphoric acid to 240°C for 1 hour, in phenol followed by heating for 1 hour at 400°C, and as a melt with the final temperature at 400°C for 1 hour. The inherent viscosity for the final polymers were 1.29 for the polyphosphoric acid run, 0.19 for the phenol run, and 0.25 for the melt run. Although high molecular weight polymer can be obtained in polyphosphoric acid, all attempts during the previous contract year and the present program to obtain high molecular weight polymer by some means applicable for using the polymer as a laminating or adhesive material have failed.

EXPERIMENTAL

POLYQUINOXALINES

Reactants

3,3',4,4'-Tetraaminodiphenyl Ether (TADE)

Acetic anhydride (5.3 l) was added to a slurry of 4,4'-oxydianiline (1000 g, 5.0 mole) in acetic acid (2 l) at ambient temperature during 5 hours. After stirring overnight, nitric acid (70%, 1260 ml) was added dropwise during 5 hours at 22°-26°C to the tan acetylation mixture, with acetic acid (6.3 l) added intermittently to improve the stirring action. After complete nitric acid addition, the thick yellow slurry was stirred for 2 hours, followed by dilution with water (2 l). After overnight stirring, filtration provided a yellow solid which was washed twice with water (5 l). The partially dried yellow solid (3,3'-dinitro-4,4'-diacetamidodiphenyl ether, mp 213°-217°C) was added to a solution of potassium hydroxide (3500 g) in methanol (6 l). The reddish-orange reaction mixture was stirred overnight, followed by neutralization with aqueous hydrochloric acid. A slurry of sodium sulfide nonahydrate (4800 g) in water (about 6 l) was added during 5 hours at about 60°C, allowing the methanol to distill off. After complete sodium sulfide addition, the greenish-brown slurry was stirred overnight at ambient temperature, and was then cooled in an ice bath. Filtration provided a tan solid which was recrystallized under nitrogen from deoxygenated water, using charcoal and a pinch of sodium hydrosulfite. Upon cooling the resulting clear yellow filtrate, near-white crystals separated which were isolated to yield 3,3',4,4'-tetraaminodiphenyl ether (620 g, 54% overall yield) as a near-white solid melting at 155.0°-155.5°C.

3,3'-Diaminobenzidine (DAB)

Commercially available 3,3'-diaminobenzidine (500 g) was recrystallized from deoxygenated water (15 l) under nitrogen, using charcoal and a pinch of sodium hydrosulfite to yield near-white crystals (355 g, 71% recovery) melting at 179.5°-180°C.

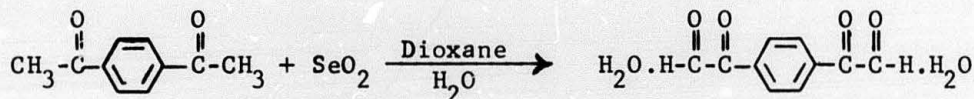
4,4'-Oxybis(phenyleneglyoxal hydrate) (OBPG)

A mixture of diphenyl ether (1532 g, 9.0 mole) and acetyl chloride (2163 g, 27.9 mole) was added at about 35°C to a stirred slurry of anhydrous aluminum chloride (3604 g, 27.0 mole) in 1,1,2,2-tetrachloroethane (6 l). The resulting dark purple reaction mixture was stirred overnight at ambient temperature, followed by pouring onto ice and hydrochloric acid. The greenish-orange organic phase was separated and washed successively with water, aqueous sodium carbonate, and water. Concentration under a water aspirator vacuum in a hot water bath provided a tan solid which was washed in a Waring blender with n-hexane. The resulting

light tan solid (2100 g, 92% yield) of 4,4'-diacetyldiphenyl ether melting at 103.5°-105°C, was added during 10 minutes to a solution of selenium dioxide (2100 g, 18.9 mole) in dioxane (12 l) and water (1.3 l) at 60°C. The dark brown reaction mixture was refluxed for 5 hours, turning black due to the precipitation of selenium. The hot reaction mixture was treated with charcoal and filtered to yield a cream-colored solid. This solid was recrystallized from a mixture of dioxane (13 l) and water (4 l) to afford white crystals (1720 g, 60% overall yield) melting at 140.5°-142°C and having the following elemental analysis:

	<u>% C</u>	<u>% H</u>
Calculated for C ₁₆ H ₁₄ O ₇ :	60.38	4.43
Found:	60.14	4.35

p-Phenylenediglyoxal Dihydrate (PG)



To a stirred solution of selenium dioxide (82 g, 0.74 mole) in dioxane (500 ml) and water (25 ml), held at 60°C was added p-diacetylbenzene (56.6 g, 0.35 mole). After 2 minutes at 60°C, the clear, light green solution had become a cloudy brick-red color. It was heated to reflux (95°C) over a 1/2-hour period and maintained at this temperature, with stirring, for 20 hours. The turbid greenish-black reaction mixture was then charcoaled and filtered hot, yielding a light yellow filtrate and a black filter cake. The insolubles were washed with hot dioxane-water and the washings combined with the main filtrate. The filtrate was concentrated to about 1/2 volume and cooled, providing an off-white product (49 g, 62.0% yield). Recrystallization from water afforded white platelets mp 157°-163°C (literature reports mp 110°-111°C for p-phenylenediglyoxal dihydrate).⁽¹⁾ Further repeated recrystallizations of small portions of the product failed to improve the melting point. However, this may be attributed to loss of water of hydration during melting, similar to that observed with p,p'-oxybis-(phenyleneglyoxal hydrate).

An elemental analysis of the white platelets (mp 157°-163°C) from the initial recrystallization was excellent for p-phenylenediglyoxal dihydrate:

	<u>% C</u>	<u>% H</u>
Calculated for C ₁₀ H ₁₀ O ₆ :	53.10	4.46
Found:	53.17	4.54

Polymers

The following procedure for the preparation of NAV-P-4 is representative of the polymerizations, NAV-P-2 were also prepared following this procedure, and the m-cresol solutions were used directly in application work.

A slurry of OBPG (636.5 g, 2.0 mole) in m-cresol (1.5 l) was added during 5 minutes to a vigorously stirred slurry of TADE (460.5 g, 2.0 mole) in m-cresol (2 l) at ambient temperature. Following the glyoxal addition, m-cresol (888 ml) was added to wash down the glyoxal and to obtain the desired concentration. The reaction mixture was stirred for 1 hour increasing the temperature from 32°C to 64°C. A clear orange-brown viscous solution formed which was stirred at 61±4°C for 1 hour. This solution which was used directly in application work contained 20% solids based upon starting material or 16.8% solids based upon the final polymer.

A small portion of the m-cresol solution was poured into a Waring blender containing methanol to precipitate a beige fibrous solid. Thorough washing with methanol followed by drying for 1 hour at 170°C under pump vacuum provided a beige polymer having an inherent viscosity (η_{inh}) of 0.66 and a polymer melt temperature (PMT) of 265°-270°C. A portion of the beige polymer in a polymerization tube under nitrogen was advanced to final polymer by introducing into a preheated oil bath at 350°C and increasing the temperature to 400°C during 1 hour. The temperature was maintained at 400°C for 1 hour. A volatile weight loss of 2.0% was recorded and an η_{inh} of 1.59 for the final polymer. During this thermal treatment, the polymer melted, foamed, and resolidified. The excellent adhesive power of the polymer was evidenced by pulling glass away from the polymerization tube during cooling.

Copolymers

NAV-P-5 Containing 25 mole-% p-Phenylenediglyoxal Dihydrate (PG)

A slurry of combined glyoxals, OBPG (28.64 g, 0.09 mole) and PG (6.79 g, 0.03 mole) in m-cresol (120 ml), was added during 7 minutes to a vigorously stirred slurry of DAB (25.71 g, 0.12 mole) in m-cresol (135 ml) at 40°C. After complete glyoxal addition, the sides of the flask were rinsed with additional m-cresol (23 ml) to obtain the desired concentration. The red slurry became increasingly more viscous as the temperature was raised from 40°C to 56°C during 35 minutes and was maintained at 54±3°C for an additional 2 hours and 40 minutes. The clear reddish-orange polymer solution was extremely viscous and was diluted with additional m-cresol (180 ml). This gave a polymer solution suitable for application, with a solids content of 12%, based on starting materials.

A small portion of the polymer solution was quenched with methanol precipitating a yellow fibrous solid. Thorough washings with methanol

followed by drying at 165°C for 3 hours under pump vacuum provided a polymer with an η_{inh} (in H₂SO₄) of 0.51 and a PMT of 295°-300°C.

A small sample of this yellow polymer was advanced to final polymer in a polymerization tube under nitrogen by introducing it into an oil bath at 360°C, heating to 400°C during 1 hour, and maintaining the tube at 404°±2°C for 1 hour. The resulting light brown foam was extremely tough and exhibited excellent glass adhesion. The volatile weight loss was 2.3% and the final polymer had an η_{inh} of 1.24.

POLYPHENYLQUINOXALINES

Reactants

4,4'-Oxybibenzil (OBB)

A mixture of diphenyl ether (715 g, 4.2 mole) and phenylacetyl chloride (1304 g, 8.4 mole) was added dropwise during 4 hours at ambient temperature to a stirred slurry of anhydrous aluminum chloride (1123, g, 8.4 mole) in carbon disulfide (3.6 l). Following complete addition, the reaction mixture thickened and solidified after stirring 0.5 hour. The carbon disulfide was removed and the solid mass broken into smaller pieces and washed in a Waring blender successively with dilute aqueous hydrochloric acid, water, aqueous sodium carbonate and water. Air drying provided a crude tan solid (1954 g) which was extracted several times with hot chloroform (total volume 8 l). Beige crystals of 4,4'-di(phenylacetylphenyl) ether (1152 g, 67% yield) melting at 174.5°-176.0°C (lit. reports mp 169°-170°C)⁽³⁾ separated from the cooled chloroform solution.

A slurry of 4,4'-di(phenylacetylphenyl) ether (788 g, 1.9 mole) in acetic anhydride (2 l) was added during 10 minutes to a stirred slurry of selenium dioxide (459 g, 4.1 mole) in acetic acid (4 l) at 60°C. The mixture which turned dark after refluxing for 5.5 hours was treated with charcoal and filtered hot. The reddish filtrate was partially concentrated and diluted with methanol to afford a yellow crystalline product (674 g) which melted at 134°C. The high melting point was attributed to incomplete oxidation therefore the yellow crystalline material (674 g) was slurried in acetic anhydride and added during 10 minutes to a stirred slurry of selenium dioxide (300 g) in acetic acid (2 l) at 60°C. The oxidation mixture was refluxed for 16 hours followed by treatment with charcoal and hot filtration. The reddish filtrate was concentrated to 2 l under water aspirator vacuum and cooled to provide a yellow crystalline solid. The yellow solid was thoroughly washed with methanol and dried to yield yellow crystals (557 g, 66% yield) of ODB melting at 108.5°-110°C (lit.⁽³⁾ reports mp 106.4°-107.4°C).

Polymers

A representative polymerization is given below for diether polyphenylquinoxaline.

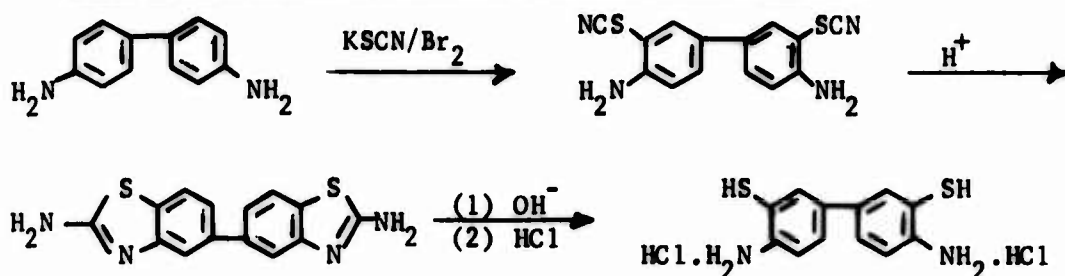
Powdered OBB (86.88 g, 0.20 mole) was added during 5 minutes to a vigorously stirred slurry of TADE (46.05 g, 0.20 mole) in *m*-cresol (400 ml) at 30°C. The reaction mixture was stirred to 54°C during 1 hour and maintained at 50°±4°C for 0.5 hour to form a clear viscous orange solution. This solution containing 21% solids, based upon starting reactants, was used directly in application work. The polymer exhibited an η_{inh} of 0.41 after isolation by quenching with methanol and drying at 170°C for 1 hour under pump vacuum. Advancement for 1 hour at 400°C under nitrogen provided a glassy yellow-brown final polymer with an η_{inh} of 1.71 and a volatile weight loss of 1.09%. It was tough and exhibited tremendous adhesion to the glass polymerization tube.

Half ether polyphenylquinoxaline was prepared following this general procedure using DAB in place of TADE. Maintaining the reaction temperature under 50°C resulted in an extremely viscous, clear orange polymer solution after only 1 hour. Isolation of a portion of this polymer followed by advancement as with the diether polyphenylquinoxaline gave a yellow final polymer with an η_{inh} of 1.91 and a volatile weight loss of 1.51%.

POLYBENZOTHAZOLES

Reactants

3,3'-Dimercaptobenzidine Dihydrochloride (DMBdiHCl)



A solution of bromine (1190 g, 7.5 mole) in acetic acid (1.5 l) was added dropwise to a vigorously stirred slurry of benzidine (340 g, 1.85 mole) and potassium thiocyanate (14.60 g, 15 mole) in glacial acetic acid (2.5 l) held at 15°C over a period of 4 hours. The resulting orange slurry was stirred overnight at ambient temperature. The orange solid (3,3'-dithiocyanobenzidine) obtained after filtration of the reaction mixture was extracted several times, each with about 10 l of hot 2% hydrochloric acid. The cooled filtrates were combined and neutralized with sodium acetate. The light yellow solid was filtered off and dried, yielding 287 g (52% yield) of 6,6'-bis(2-aminobenzothiazole).

Ring cleavage was accomplished by stirring the 6,6'-bis(2-aminobenzothiazole) under nitrogen in refluxing 50% potassium hydroxide (2.25 l) for 48 hours. After this time it had dissolved, forming a clear light yellow

solution. An additional 1.5 l of hot deoxygenated water was added and the solution was filtered hot. The cooled clear light yellow filtrate was added under nitrogen to a vigorously stirred solution of diluted hydrochloric acid at 10°-15°C, precipitating a white solid. The solid was filtered, dissolved and precipitated once more. It was then recrystallized from 2% deoxygenated hydrochloric acid yielding light yellow 3,3'-dimercaptobenzidine dihydrochloride, 240 g (41% overall yield) having the following elemental analysis:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% Cl</u>
Calculated for $C_{12}H_{14}S_2N_2Cl_2$:	44.86	4.39	8.72	19.96	22.07
Found:	44.71	4.31	8.96	20.23	21.90

3-Amino-4-mercaptobenzamide

Following the procedure outlined in the 1966 Final Report⁽¹⁾ 3-nitro-4-chlorobenzamide was reacted with sodium sulfide to yield bis(2-nitro-4-carbamylphenyl) disulfide (III) melting at 259°-262°C and having the following elemental analysis:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>
Calculated for $C_{14}H_{10}N_4O_6S_2$:	42.62	2.56	14.21	16.26
Found:	42.40	2.69	14.38	16.09

The disulfide was hydrogenated at 50 psi in methanol, using platinum dioxide catalyst to provide a quantitative yield of crude 3-amino-4-mercaptobenzamide (IV) melting at 140°-143°C. Two recrystallizations from a mixture of ethyl acetate and n-hexane under nitrogen provided pale yellow crystals melting at 153°-154°C (sealed tube).

Polymer

AA-BB Polymer

To deoxygenated polyphosphoric acid (100 g) under nitrogen, DMBdiHCl (3.213 g, 0.01 mole) was added at 75°C followed by stirring during 2 hours to 180°C to form a clear pale yellow solution. Isophthalic acid (1.661 g, 0.01 mole) was added deepening the color to a fluorescent green and the temperature was increased to 215°C during one hour and held at 210°±5°C with stirring for 16 hours. The brownish-green, very viscous solution was heated to 245°C for 1 hour then poured into hot water in a Waring blender precipitating a greenish-brown fibrous solid. The solid was successively washed with water, 10% sodium hydroxide, and water followed by drying at 100°C for 4 hours under pump vacuum. The resulting green polymer displayed an η_{inh} of 1.45.

To deoxygenated N,N-diethylaniline (150 ml) at 130°C under nitrogen, DMBdiHCl (6.425 g, 0.020 mole) was added to form a clear yellow solution.

Diphenyl isophthalate (6.366 g, 0.020 mole) was added with N,N-diethylaniline (50 ml) as wash and the clear yellow reaction mixture refluxed (218°C) for 20 hours to precipitate a yellow solid. Concentration of the reaction mixture to about 80 ml by distillation followed by diluting the cooled residue with n-hexane provided a yellow prepolymer with a PMT of 95°-100°C. A portion of the prepolymer was advanced under nitrogen to final polymer by heating from 230°C to 400°C during 1.5 hour and maintaining at 400°C for 1 hour. The resulting yellow polymer exhibited an η_{inh} of 0.69. Following this procedure, a prepolymer was prepared from DMBdiHCl (160.64 g, 0.50 mole) and diphenyl isophthalate (159.16 g, 0.50 mole) in N,N-diethylaniline (638 ml). The resulting prepolymer exhibited a PMT under pressure of 220°C-230°C. When this prepolymer was used in laminate fabrication, poor wetting of the glass cloth was observed. The prepolymer exhibited an η_{inh} of 0.13 and a volatile content of 9% which indicated that the prepolymer had been advanced too far to provide good flow properties. Conversion to final polymer by heating at 400°C for 1 hour under nitrogen provided a yellow polymer with an η_{inh} of 0.47.

In deoxygenated polyphosphoric acid (100 g) under nitrogen, DMBdiHCl (3.213 g, 0.010 mole) was added at 70°C followed by stirring during 1 hour to 120°C to form a clear yellow solution. Isophthalamide (1.642 g, 0.010 mole) was added at 120°C and the temperature increased and stirred at 215°C for 16 hours followed by stirring for 1 hour at 245°C. The resulting clear brownish-green solution was poured into hot water in a Waring blender to precipitate a green solid. The solid was washed successively with water, aqueous sodium hydroxide, and water followed by drying at 170°C for several hours under pump vacuum. The greenish polymer exhibited an η_{inh} of 1.07.

A-B Polymer



3-Amino-4-mercaptobenzamide was polymerized under nitrogen in commercial grade polyphosphoric acid to 240°C for 1 hour, in phenol followed by heating for 1 hour at 400°C, and as a melt with the final temperature at 400°C for 1 hour. The η_{inh} (0.5% H₂SO₄ at 25°C) for the final polymers were 1.29 for the polyphosphoric acid run, 0.19 for phenol run, and 0.25 for the melt run. Although high molecular weight polymer can be obtained in polyphosphoric acid, all attempts to date to obtain high molecular weight polymer by some means applicable for using the polymer as a laminating or adhesive material have failed. Therefore, at the midpoint of this program, effort on this polymer was suspended.

CONCLUSIONS

Potential was definitely established for polyquinoxalines as laminating resins and structural adhesives on glass fabric reinforcements.

The data showed that, in addition to being more readily synthesized, the NAV-P-2 system gave somewhat better results than NAV-P-4.

All future work with polyquinoxalines should involve the NAV-P-2 system.

Some slight thermoplasticity exists in NAV-P-2 which must be overcome.

Although excellent adhesive data were obtained, curing temperatures and pressures should be reduced.

The polyquinoxalines have outstanding processability, hence are promising for unidirectional composites with high-modulus filaments.

The phenyl-substituted polymers, NAV-P-10 and NAV-P-11, show superior isothermal oxidative stability, but their sufficiently severe thermoplastic behavior requires a significant increase in the glass transition temperature.

Both NAV-P-10 and NAV-P-11 possess definite promise since they provided over 100,000 psi in flexure at room temperature.

NAV-P-2 showed definite potential as a fiber.

NAV-P-10 and NAV-P-2 were completely stable in the presence of high temperature explosives at 260°C and thus can be considered for certain applications.

RECOMMENDATIONS

Work with NAV-P-2 should be concentrated on the use of high-modulus fibers other than boron for reinforcement.

The structure of NAV-P-2 should be modified to provide higher glass transition temperatures to overcome thermoplasticity. A copolymer approach, using varying amounts of p-phenylene bisglyoxal, seems most direct.

Increases in glass transition temperature are especially needed for NAV-P-10 type polymers if they are to achieve mechanical properties at elevated temperatures concomitant with their improved isothermal aging stability.

Efforts on the NAV-P-20 type polymers should be temporarily suspended in favor of other work (see below).

The unusually good processability of NAV-P-2 polymers should be followed up by a preliminary investigation into approaches to polyquin-oxaline step-ladders and ladder structures.

Unclassified

Security Classification

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13. ABSTRACT <p>The work described in this report covers the period of 8 June 1967 through 8 May 1968. Polyquinoxalines were shown to have outstanding processability which enables fabrication of laminates having resin matrices with reduced porosity. Excellent laminate and adhesive data were obtained after 200 hours at 600°F or 50 hours at 700°F, both in air and tested at temperature. Initial efforts provided encouraging results on unidirectional composites, using high modulus fibers. Some polymer modification is necessary to remove slight thermoplasticity. Polyphenylquinoxalines are definitely more stable than polyquinoxalines, when tested under isothermal conditions and demonstrate excellent processability. A sharp increase in glass transition temperature is necessary to exploit this improved stability. Two polyquinoxalines were tested for compatibility with ONT and HNS II heat resistant explosives at 260° C. Both samples were found to be very compatible. Samples of both polyquinoxalines were submitted for tests as a potential fiber. Both could be formed into fibers having interesting high temperature properties; the half ether has somewhat better. Polybenzothiazoles continued to provide problems in monomer purity.</p>		

DD FORM 1473

Unclassified

Security Classification

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polyquinoxalines						
Polyphenylquinoxalines						
Polybenzothiazoles						
High Temperature Stable Laminates						
Adhesives						
High Modulus Fibers						
Heat Aging Resistance						